



# JOURNAL

OF

## THE CHEMICAL SOCIETY

CONTAINING

PROCEEDINGS, PAPERS COMMUNICATED TO THE SOCIETY,

AND

ABSTRACTS OF CHEMICAL PAPERS.

Vols. 117 &amp; 118.

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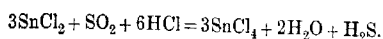
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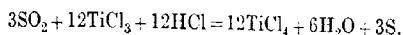
# CXXIV.—*The Oxidising Properties of Sulphur Dioxide.* *Part I. Iron Chlorides.*

By WILLIAM WARDLAW and FRANCIS HERBERT CLEWS.

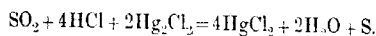
As this paper has to deal with the reactions of sulphur dioxide and metallic chlorides, it may be well to summarise our present knowledge relative to this subject. The oxidation of stannous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid has been shown (Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1914, **5**, 187) to proceed quantitatively to completion according to the equation



Sulphurous acid is reduced by titanous chloride to hyposulphurous acid (Knecht, *Ber.*, 1903, **36**, 166), and its further reduction to sulphur was noticed by the same investigator. Smythe and Wardlaw (*loc. cit.*) further proved that when sulphur dioxide is passed into a warm, strongly acid solution of titanous chloride hydrogen sulphide is freely evolved. Sulphur is formed by secondary reaction between the hydrogen sulphide and the sulphur dioxide, and if the escaping hydrogen sulphide is led into an excess of sulphur dioxide in concentrated hydrochloric acid, the reaction which goes to completion may be quantitatively summarised as follows:



The same authors (*loc. cit.*) have shown that sulphur dioxide oxidises mercurous chloride in the presence of concentrated hydrochloric acid according to the equation



In the same paper it was mentioned that in concentrated hydrochloric acid, ferrous chloride is oxidised by sulphur dioxide to ferric chloride, with the formation of sulphur. No sulphuric acid was detected in the solution. This reaction differed from those already quoted in that oxidation under the most favourable conditions proceeded only to a limited extent, the average yield of ferric iron in all the experiments being 7 per cent. of the total iron present, the extremes being 4 and 11.6 per cent. In these experiments, rigid control was not exercised over the conditions of temperature, concentration, etc., and it seemed desirable, therefore, that a systematic investigation of this reaction should be carried out.

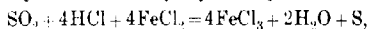


## EXPERIMENTAL.

The general method of procedure was as follows. Pure electrolytic iron was dissolved in pure concentrated hydrochloric acid contained in a flask made entirely of glass, and such that the reacting gases could be passed through the solution contained in it. This was connected with wash-bottles containing water and sodium hydroxide solution respectively. These served to absorb the effluent sulphur dioxide and hydrogen chloride and to exclude air, and so prevent atmospheric oxidation. The temperature of the flask was controlled by immersion in an oil-bath. A stream of carbon dioxide was continuously passed through the apparatus during the solution of the metal. When the iron had completely dissolved, the flask was connected with a sulphur-dioxide syphon and the gas passed for a stated period. It was noticed that after the sulphur dioxide had passed for a few minutes the solution changed to olive-green, then to reddish-brown, and became distinctly opalescent, owing to the separation of sulphur. After the reaction had proceeded for the required time, the sulphur dioxide was displaced by carbon dioxide, the solution cooled in a stream of the same gas, and the iron titrated, after suitable dilution with air-free water, with standard potassium dichromate according to Zimmermann and Reinhardt's method. The sulphur was determined by filtration and direct weighing.

*Quantitative Aspect of the Reaction.*

There are two possible reactions involved, corresponding (a) with direct reduction of the sulphur dioxide to sulphur, and (b) with initial reduction of the sulphur dioxide to hydrogen sulphide, which reacts with excess of sulphur dioxide, forming sulphur. Both reactions are represented, finally, by the equation



so that it is impossible to decide quantitatively between the two. Moreover, owing to the fact that the limit of reaction has been shown to be so soon reached, the accurate estimation of the small quantity of sulphur is very difficult.

The following are examples of the results obtained by Smythe and Wardlaw (*loc. cit.*).

TABLE I.

Experiment.	Concentration of ferrous solution.	Ferric iron produced. Gram.	Sulphur.	
			Found. Gram.	Calc. Gram.
1	5.893 grams Fe per 100 c.c.	0.683	0.062	0.098
2	4.458 „ „ 200 c.c.	0.392	0.040	0.056
3	5.450 „ „ 200 c.c.	0.340	0.035	0.048

The conclusion to be drawn is that the equation mentioned above represents the reaction. From general considerations, one is also led to infer that it undoubtedly follows the course (a). Although hydrogen sulphide has never been directly detected in the reaction, from the fact that sulphur is formed in the neck of the flask and in the outlet tubes, it is possible that the reaction follows the course (b) to a very limited extent.

*Influence of Concentration of Total Iron.*

A range of concentrations of iron was investigated by dissolving varying quantities of iron (1—10 grams) in 250 c.c. of concentrated hydrochloric acid. Sulphur dioxide was passed through the solution for four hours at 115°, and the amount of ferric salt subsequently determined by titration.

TABLE II.

Experiment.	4.	5.	6.	7.	8.
Grams of iron dissolved in 250 c.c. of acid .....	1	3	5	7	10
Ferric iron per cent. ....	5.3	4.2	3.4	3.3	3.6

These results tend to show that the limit of oxidation is not influenced by the initial concentration of the iron. The concentration of the hydrochloric acid is not exactly constant in these experiments, owing to the varying losses of hydrogen chloride during the solution of the different quantities of metal, and this undoubtedly influences the degree of oxidation.

TABLE III.

*Influence of Temperature.*

*Concentration.*—Two grams of iron in 100 c.c. of concentrated hydrochloric acid.

*Duration of Experiments.*—Two and a-half hours.

Experiment .....	9.	10.	11.	12.	13.	14.	15.
Temperature .....	61°	70	79	93	115	125	gently boiling.
Ferric iron per cent....	1.6	3.0	3.5	5.2	3.8	3.0	2.8

The existence of an optimum temperature (approximately 95°) is the result of two or more opposing factors. The reaction-velocity will be favoured by an increase in temperature, whilst the higher temperature will lead to a more rapid loss of hydrochloric acid,

especially in the early stages of the reaction. It is also highly probable that the solubility of the sulphur dioxide decreases with rise in temperature.

*Influence of the Concentration of Hydrochloric Acid.*

The three following experiments are modifications of those described in table III with a view to change the concentration of hydrochloric acid. Values from table III are added for comparison.

TABLE IV.

*Concentration.*—Two grams of iron dissolved in 100 c.c. of concentrated hydrochloric acid.

*Duration of Experiment.*—Two and a-half hours.

Ex- peri- ment.	Description.	Tem- pera- ture.	Ferrie iron Total iron $\times 100$ .	From Table III. Ferrie iron. Per cent.
16	Sulphur dioxide passed through concentrated hydrochloric acid at 95° before being led into the ferrous chloride solution .....	95°	7.8	5.2
17	Mixture of hydrogen chloride and sulphur dioxide (60 per cent. of HCl by weight)* passed into ferrous chloride solution .....	115	4.7	3.8
18	Carbon dioxide passed through ferrous chloride solution at 115° for 30 minutes and then sulphur dioxide for 2½ hours .....	115	1.3	3.8

\* In all cases the composition of gaseous mixtures of sulphur dioxide and hydrogen chloride will be expressed by the percentage of each constituent by weight.

The increased yields in experiments 16 and 17, and diminished yield in experiment 18, in which excess of hydrochloric acid is removed from the solution, show that the oxidising effect of sulphur dioxide is only appreciable at concentrations exceeding that of the mixture of constant boiling point.

Accordingly, in the next experiments (table V) iron was dissolved in hydrochloric acid diluted to the concentration of the mixture of constant boiling point, and a mixture of hydrogen chloride and sulphur dioxide in different proportions passed into the ferrous chloride solution.

The ratio of sulphur dioxide to hydrogen chloride was observed by diverting a small proportion of the gases, by means of a T-piece, while the experiment was in progress. The acid gases were absorbed in 50 c.c. of *N*-sodium hydroxide, the chloride being sub-

sequently titrated with standard silver nitrate and ammonium thiocyanate, and the sulphite with standard iodine and sodium thiosulphate.

TABLE V.

*Concentration.*—Two grams of iron dissolved in 100 c.c. of hydrochloric acid (22 per cent. HCl).

*Duration of Experiment.*—Four hours.

*Temperature.*—115°.

Experiment.	Percentage composition of mixed gases.		$\frac{\text{Ferric iron}}{\text{Total iron}} \times 100.$
	SO <sub>2</sub> .	HCl.	
19	81.7	18.3	2.3
20	56.7	43.3	2.2
21	22.5	77.5	4.2
22	15.8	84.2	8.6
23	10.1	89.9	3.9

The results show that for the conditions described in the above experiments there is a comparatively narrow range of composition between 10 and 20 per cent. of sulphur dioxide which is most favourable for the oxidation of ferrous chloride, a maximum being reached in the neighbourhood of 16 per cent. of sulphur dioxide.

*Limiting Concentration of Hydrochloric Acid for Oxidation of Ferrous Chloride by Sulphur Dioxide.*

Since in dilute hydrochloric acid solution sulphur dioxide completely reduces ferric chloride to ferrous chloride, there will be

TABLE VI.

*Temperature.*—95°.

*Duration of Experiment.*—Four hours.

*Solution.*—Five grams of iron dissolved in acid specified in columns 2 and 3.

Experi- ment.	Concentrated hydrochloric acid. c.c.		Water. c.c.	Free HCl in 1000 c.c. of solution. Gram.	Remarks.
40	160	+	90	210.5	Little oxidation; about 0.5 per cent.
41	140	+	110	179.3	Very little oxidation; not measured.
42	130	+	120	165.8	Minute oxidation as shown by sulphur deposit.
43	125	+	125	165.1	No oxidation as shown by sulphur deposit.

some concentration of acid below which it is impossible to observe the oxidation of ferrous chloride by sulphur dioxide.

Iron was dissolved in acids of different concentrations, and the action of sulphur dioxide for four hours at 95° was observed.

For the analysis, a portion of the solution was withdrawn, weighed, and, after removal of the sulphur dioxide, diluted to a convenient volume. The iron and total chloride were determined, and from the difference the "free" hydrochloric acid was calculated. The specific gravity of the remainder of the solution was determined in order to state the concentration in grams per litre (see table VI).

It is concluded that oxidation by sulphur dioxide does not occur in ferrous chloride solutions containing less than 165 grams per litre of "free" hydrogen chloride.

*Limit of Oxidation of Ferrous Chloride by Sulphur Dioxide in Hydrochloric Acid Solution.*

(a) *Experiments at Atmospheric Pressure.*—With the purpose of determining the limit of oxidation, use was made of a rather larger flask fitted with a water-cooled exit tube, and containing an amount of solution sufficient to provide two samples for analysis.

Five grams of iron dissolved in 250 c.c. of concentrated hydrochloric acid (33 per cent.) were treated with hydrogen chloride and sulphur dioxide at 115°, as described in the following experiments.

TABLE VII.

Experiment.	Description.	Time of taking sample from commencement of experiment.	
		Ferric iron	Total iron
24	Hydrogen chloride and sulphur dioxide (80 and 20 per cent.) passed continuously into ferrous chloride solution.	4 hours	2.2
		8 "	3.0
25	Hydrogen chloride and sulphur dioxide (50 per cent.) passed into ferrous chloride solution.	4 "	4.3
		6½ "	4.1
26	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (50 per cent.) continuously.	4 "	4.8
		8 "	4.7
27	Sulphur dioxide alone passed for half an hour, then hydrogen chloride and sulphur dioxide (80 and 20 per cent.)	3 "	3.5
		6½ "	7.1

TABLE VII (continued).

Experi- ment.	Description.	Time of taking sample from commence- ment of experiment.	Ferrie iron Total iron $\times 100$ .
28	*The ferrous chloride solution was alternately cooled to 30° (1-hour) and then quickly raised to 115° (heated for 2 hours), hydrogen chloride and sulphur dioxide (50 per cent. of each) passed continuously).	3 hours	6.5
		6 "	7.0
29	Experiment 28 repeated but cooled for 1 hour and heated to 115° for 1 hour.	6 "	8.8

\* This procedure enabled the solution to absorb a large amount of the gases at the lower temperatures. On rapidly raising the temperature to 115° the solubility values would not be attained immediately, and during this interval the temporarily increased concentration of hydrochloric acid and sulphur dioxide would be available for reaction with the ferrous salt.

An oxidation of 8.8 per cent. (in experiment 29) is the highest obtained by the action of sulphur dioxide on ferrous chloride operating under a pressure slightly in excess of the atmospheric.

(b) *Experiments with Sealed Tubes.*—A rather higher degree of oxidation was obtained by the use of a sealed tube.

*Expt. 30.*—Half a gram of iron was dissolved in 10 c.c. of concentrated hydrochloric acid in a Carius tube in a current of carbon dioxide. The tube was immersed in ice, the solution saturated with sulphur dioxide, and the tube sealed. It was then heated at 100° for six hours and allowed to cool overnight. Titration showed that oxidation had occurred to the extent of 9.5 per cent., a value only slightly in excess of those obtained under normal pressures.

#### *Limit of Reduction of Ferric Chloride by Sulphur Dioxide in Concentrated Hydrochloric Acid Solution.*

(a) *Experiments under Atmospheric Pressure.*—It is well known that excess of hydrochloric acid prevents the complete reduction of ferric chloride by sulphur dioxide (Treadwell and Hall, "Quantitative Analysis," 5th ed., p. 607, footnote). It was not known, however, to what concentration of hydrochloric acid this referred or the extent to which ferric chloride was reduced.

Since the reduction of ferric chloride in concentrated hydrochloric acid was found to proceed slowly, mixtures of ferrous and ferric chlorides were prepared and their compositions determined,

both before and after passing sulphur dioxide and hydrogen chloride (approximately 50 per cent. of each gas) for a definite time. By this means, the value to which the reduction would eventually attain was estimated.

TABLE VIII.

*Concentration.*—Five grams of iron in 250 c.c. of hydrochloric acid (33 per cent.).

*Temperature.*—115°.

*Gas.*— $\text{SO}_2 + \text{HCl}$  (50 per cent. mixture).

Experi- ment.	Duration of experiment. Hours.	Ferric iron Total iron $\times 100$ .		Reduction gradient (average reduction per hour).	Remarks.
		Initial value.	Final value.		
31	4.0	100.0	78.2	5.4	Sulphate formed.
32	4.0	72.2	68.3	0.98	"
33	6.3	53.8	48.5	0.84	"
34	4.0	42.1	39.3	0.70	"
35	6.0	20.7	18.3	0.40	"
36	2.5	18.3	18.3	—	"
37	5.6	10.8	10.7	—	No sulphate.

No sulphur was formed in any of the above experiments. Apparently iron solutions containing more than 18.3 per cent. of ferric iron are slowly reduced by sulphur dioxide in the presence of concentrated hydrochloric acid. There seems also to be a range of from 10 to 18.3 per cent. of ferric iron in which there is no evidence of reduction or oxidation by the sulphur dioxide during the time of the experiments. Evidently this represents a zone in which the rate of reaction of the sulphur dioxide is very slow.

The solution in experiment 37 was analysed, and it was shown to contain in 1 litre 239 grams of "free" hydrochloric acid and 0.314 gram of sulphur dioxide.

(b) *Experiments in Sealed Tubes.*—Five grams of ferric chloride were dissolved in 10 c.c. of hydrochloric acid (33 per cent.), and the solution was saturated with sulphur dioxide at 0°. The tube was sealed and heated to 110° for four hours. Analysis showed a reduction of 20.6 per cent., and sulphuric acid was detected in the solution. A similar experiment after twenty-five hours at 110° gave only 22.3 per cent. of reduction. Apparently the high concentration of hydrochloric acid which exists in a closed vessel inhibits the reduction by sulphur dioxide, just as a high concentration of acid appears also to favour the oxidation of ferrous chloride.

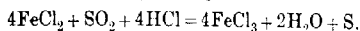
*Reduction of Ferric Chloride by Sulphur.*

Stokes (*Bull. U.S. Geol. Survey*, No. 186, 1901) has examined the action of pyrites and marcasite on a hot dilute solution of ferric chloride, and observed reduction to a considerable extent (65 per cent. of the sulphur), the sulphur being oxidised to sulphuric acid. The present authors find that the action of sulphur in concentrated hydrochloric acid on ferric chloride is slight.

A solution of 5 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid was boiled in an atmosphere of carbon dioxide for one and a-half hours. The reduction corresponded with 0.65 per cent., the sulphur being oxidised to sulphuric acid. A solution of 3 grams of ferric chloride in 50 c.c. of concentrated hydrochloric acid to which 50 c.c. of colloidal sulphur solution were added, on boiling for one and a-half hours resulted in 1.7 per cent. of reduction. Sulphuric acid was produced. Experiments on the lines of those shown in table VIII, in which a proportion of finely divided sulphur was added, showed that it exerted very little reducing action in comparison with the sulphur dioxide.

*Summary.*

(1) The oxidation of ferrous chloride by sulphur dioxide can be represented quantitatively by the equation



(2) The degree of oxidation is independent of the initial concentration of total iron.

(3) The most favourable temperature for the oxidation by sulphur dioxide of a solution of ferrous chloride in 33 per cent. hydrochloric acid is 95°.

(4) Oxidation by sulphur dioxide at 95° does not occur in solutions of ferrous chloride containing less than 165 grams per litre of "free" hydrogen chloride.

(5) A solution of ferrous chloride in hydrochloric acid of constant boiling point (22 per cent.) at 115° gave a maximum oxidation of 8.6 per cent. (ferric iron) when treated with a mixture of sulphur dioxide and hydrogen chloride containing 16 per cent. of sulphur dioxide.

Mixtures containing 10 to 20 per cent. of sulphur dioxide are most favourable for oxidation under the above conditions.

(6) The highest percentage of ferric iron obtained in any of the flask experiments recorded in this paper was 8.8. This result was produced by treatment of a ferrous chloride solution in 33 per cent.



hydrochloric acid at 115° with a 50 per cent. mixture of sulphur dioxide and hydrogen chloride under special conditions.

(7) Sealed-tube experiments gave a maximum oxidation of 9.5 per cent. of ferric iron.

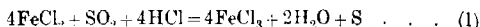
(8) Iron solutions containing 10 to 18.3 per cent. of ferric iron in 33 per cent. hydrochloric acid at 115° showed no evidence of oxidation or reduction when a 50 per cent. mixture of sulphur dioxide and hydrogen chloride was passed into them for varying periods.

(9) Under the same experimental conditions as in (8), iron solutions containing more than 18.3 per cent. of ferric iron were slowly reduced.

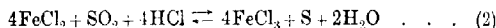
(10) Ferric chloride in concentrated hydrochloric acid was reduced to a small extent by sulphur.

#### *Theoretical.*

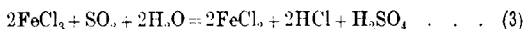
The oxidation of a ferrous chloride solution by sulphur dioxide has been shown to be quantitatively represented by the equation



Moreover, since sulphur is able to reduce ferric chloride to some extent, it seems justifiable to assume that the above equation is reversible.



This fact is generally obscured, however, by the more general equation

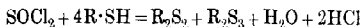


Since no sulphuric acid is detected when a pure ferrous chloride solution is oxidised by sulphur dioxide in the presence of concentrated hydrochloric acid, it can be assumed that under these conditions the reaction that occurs is solely represented by equation (2). Moreover, seeing that sulphuric acid is only detected when sulphur dioxide in the presence of concentrated hydrochloric acid reacts with iron solutions containing more than 18.3 per cent. of ferric iron, it appears that reaction (3) is only operative in such solutions.

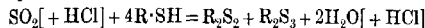
The idea that a reversible reaction takes place when pure ferrous chloride solution is oxidised by sulphur dioxide receives added support from the fact that only a limited yield of ferric salt is possible, and that the reaction is not greatly influenced by the initial concentration of total iron. Applying the law of mass action to equation (2), it appears that for a given concentration of sulphur dioxide and hydrogen chloride the equilibrium position would be

determined solely by the ratio of ferrous to ferric iron, assuming that the active masses of the sulphur and water are constant. The importance of a high concentration of hydrogen chloride to bring about the oxidation also follows logically from the idea of a balanced reaction.

The dependence of sulphur dioxide as an oxidising agent on a high concentration of hydrochloric acid has led to the suggestion that hydrochloric acid and sulphur dioxide interact, forming thionyl chloride to a small extent (Smythe and Wardlaw, *loc. cit.*). This idea receives support from the following reactions with the mercaptans:

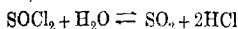


(Holmberg, *Annalen*, 1908, **359**, 81),

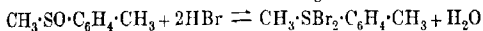


(Smythe and Forster, T., 1910, **97**, 1195).

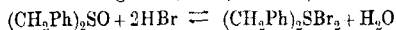
On this assumption, the reaction



must be reversible. Although this has not been proved directly, there is some indirect evidence in that when thionyl chloride reacts with mercaptans at low temperatures ( $0^\circ$  to  $-70^\circ$ ), hydrogen chloride and sulphur dioxide are evolved, and water is found among the residual products (Tasker and Jones, T., 1909, **96**, 1904, 1910). In addition, the reactions of the sulfoxides and the haloid acids are to some extent analogous.



(Zincke and Frohneberg, *Ber.*, 1910, **43**, 837),



(Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75).

From this idea, the question arises as to whether the oxidising properties of sulphur dioxide are only operative in the presence of concentrated hydrochloric acid. Experiments have been in progress to determine this point, and the results will be communicated in a further paper.

THE UNIVERSITY,  
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[Received, August 12th, 1920.]

CXXV.—*The Hydrolysis of Platinum Salts. Part I.  
Potassium Platinichloride.*

By EBEN HENRY ARCHIBALD.

WHILE carrying out a series of experiments on the solubility of potassium platinichloride (Archibald, Wilcox, and Buckley, *J. Amer. Chem. Soc.*, 1908, **30**, 747), it was noticed that this salt undergoes hydrolysis in aqueous solutions at the ordinary temperature. Some time later, while studying the conductivity of some platinum compounds (Archibald and Patrick, *ibid.*, 1912, **34**, 369), it was found that this hydrolytic decomposition proceeded much more rapidly when the solutions were exposed to the action of light. As the extent to which this reaction has taken place in any given time could be measured very accurately, whilst the rate at which it proceeded was sufficiently slow to allow of a number of measurements being made with any one solution—a condition that is satisfied by very few inorganic salts—it was thought worth while to make a somewhat extended study of the hydrolysis of this salt under different conditions as to (1) dilution; (2) the presence of other chlorides and neutral salts; (3) the reversibility of the reaction.

*Previous Observations regarding this Hydrolysis.*

The action of light on potassium platinichloride appears to have been first noted by Sonstadt (*P.*, 1898, **14**, 25). He states that light has the same effect on very dilute solutions of the salt as heat. A solution containing 1 part of salt in 10,000 parts of water became turbid when heated for an hour or two. He observed no effect in the case of more concentrated solutions, and seems to have judged the extent of the reaction from the appearance of the solution and the formation of a sediment, considered to be platinum monochloride.

It is of interest here to refer to a letter of Sir John Herschel to Dr. Daubeny, written in 1832 (*Phil. Mag.*, 1832, [iii], **1**, 58). This letter states that if a solution of platinum in nitromuriatic acid, in which the excess of acid has been neutralised by the addition of lime, this being followed by filtration, is mixed with water in the dark, no precipitation takes place for a very long while, but if the mixture is exposed to sunlight it instantly becomes milky and a copious precipitate forms. The writer of the letter further showed that this effect was confined to the violet end of the spectrum, no action taking place when tubes containing the

platinum solutions were immersed in red- or yellow-coloured solutions and then exposed to the sunlight.

That light greatly accelerates the hydrolytic decomposition of platinum tetrachloride seems to have been generally recognised. Kohlrausch found that the conductivity of aqueous solutions of this compound increased much more rapidly when under the influence of light than when kept in the dark. The presence of the platinum electrodes also increased the velocity of the reaction. Solutions of chloroplatinic acid more concentrated than  $N/10$  were apparently not affected by light.

#### EXPERIMENTAL.

##### *Preparation of Materials.*

*Hydrochloric Acid.*—The hydrochloric acid used was prepared by heating concentrated hydrochloric acid and passing the liberated gas into distilled water, the first and last parts of the distillate being rejected.

*Potassium Chloride.*—Commercial potassium chloride was recrystallised several times from water saturated with hydrogen chloride, finally from pure water. Portions so obtained were washed free of mother liquor and dried at a high temperature.

*Potassium Platinichloride.*—In preparing the chloroplatinic acid from which the platinichloride was obtained, platinum scrap was freed of surface impurities, then boiled for some time in concentrated hydrochloric acid. The platinum was then dissolved in aqua regia and the solution evaporated almost to dryness, after adding concentrated hydrochloric acid. After again adding hydrochloric acid and evaporating a second time, the residue was dissolved in water containing hydrochloric acid, and the platinum precipitated from this by adding a solution of ammonium chloride. The resulting ammonium platinichloride was collected in a Gooch filter, washed with alcohol and water, and dried in an air-bath at a low temperature. The dry salt was then reduced by heating in a current of hydrogen, and the platinum-black formed was well washed in water.

In order to ensure the absence of any nitric acid from the final preparation, the platinum-black was dissolved according to the method suggested by Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 29) and modified by the author (*Zeitsch. anorg. Chem.*, 1910, **66**, 169). According to this method, the platinum-black is made the anode in the lower part of a glass tube, about 2 cm. in diameter, containing concentrated hydrochloric acid as electrolyte. At the anode the chlorine attacks the platinum, forming platinum chloride, and the resulting chloroplatinic acid falls to the bottom and can

be drawn off through a siphon sealed to the bottom of the main tube. The solution prepared in this way is somewhat diluted, and the platinum then precipitated by adding slowly a solution of a portion of the purified potassium chloride. The precipitated platinichloride, after being washed and dried, is ready for use.

#### *Apparatus.*

The graduations on the pipettes and burettes were tested by weighing the water delivered, allowance being made for air-displacement and the temperature of the water. In the case of the flasks, a graduation mark was made at that point on the stem at which the flask contained water sufficient to balance brass weights equal to the apparent weight of a kilogram or 100 grams, as the case might be, of water weighed in air at 20°.

The weights were corrected by the method suggested by Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

#### *Method of Measuring the Extent of the Hydrolytic Action.*

As hydrochloric acid is formed as the hydrolysis proceeds, the rate at which the reaction takes place and the extent to which it has proceeded at any given time can be measured by titrating a known volume of the solution with a standard solution of an alkali, such as barium hydroxide. Among several indicators tried, such as methyl-red, methyl-orange, cochineal, and phenolphthalein, none appeared superior to phenolphthalein. The colour reaction with this substance was distinct and delicate. With the burettes employed in this work, the error in reading the volume delivered did not exceed 0.02 c.c., and this, with the strength of solution employed as standard, corresponded with 0.0000078 gram of hydrogen chloride.

The solutions first studied contained  $\frac{K_2PtCl_6}{100} = 4.864$  grams,  $\frac{K_2PtCl_6}{200} = 2.432$  grams,  $\frac{K_2PtCl_6}{400} = 1.216$  grams, and  $\frac{K_2PtCl_6}{800} = 0.6080$  gram of potassium platinichloride in a litre of solution. In terms of equivalent gram-molecules of platinum chloride they were, respectively,  $N/25$ ,  $N/50$ ,  $N/100$ , and  $N/200$ . These solutions were prepared by weighing the required amount of salt in each case; the necessary water was added in the dark, and the solution carefully protected from the light until everything was in readiness to begin a series of measurements. The velocity of the hydrolytic reaction was so low, even for the most concentrated solution studied, that the time required to dissolve the platinum salt need not be considered in any of the measurements. The

initial acidity was now measured—this was seldom equivalent to more than 0.05 c.c. of the standard for a 10.0 c.c. portion of the platinum solution. The vessels containing the solutions were then immersed in water-baths contained in glass tanks, and here exposed, at a certain distance, to the radiations from a 300-watt lamp. The temperature of the bath was maintained constant within  $0.5^{\circ}$  by means of a system of tubes, through which water circulated. An ammeter reading to 0.001 ampere was placed in series with the lamp, and by means of a voltmeter the energy being used was measured at frequent intervals. From time to time, 10 c.c. portions of the platinum solutions were withdrawn by means of a pipette, and the acidity was titrated against the standard alkali. The results obtained for the above four solutions are given below.

The figures in the first column indicate the time, in minutes, during which the solution has been exposed to the light. The second column shows the number of c.c. of alkali necessary to neutralise a 10 c.c. portion of the platinum solution. The third column contains the weight, in grams, of hydrogen chloride formed in 100 c.c. of solution.

TABLE I.

<i>N/200-K<sub>2</sub>PtCl<sub>6</sub> Solution.</i>			<i>N/100-K<sub>2</sub>PtCl<sub>6</sub> Solution.</i>		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
5	0.04	0.00015	40	0.20	0.00078
20	0.10	0.00039	125	0.40	0.00156
40	0.14	0.00054	265	0.74	0.00288
65	0.20	0.00073	410	1.34	0.00495
125	0.32	0.00125	580	1.92	0.00749
215	0.54	0.00210	955	3.00	0.01174
265	0.64	0.00249	1455	3.96	0.01544
400	1.08	0.00421	1810	4.14	0.01615
580	1.72	0.00671	1900	4.20	0.01638
945	2.34	0.00913	2150	4.24	0.01653
1736	3.06	0.01193	2750	4.29	0.01673
2200	3.30	0.01287			
2900	3.35	0.01365			

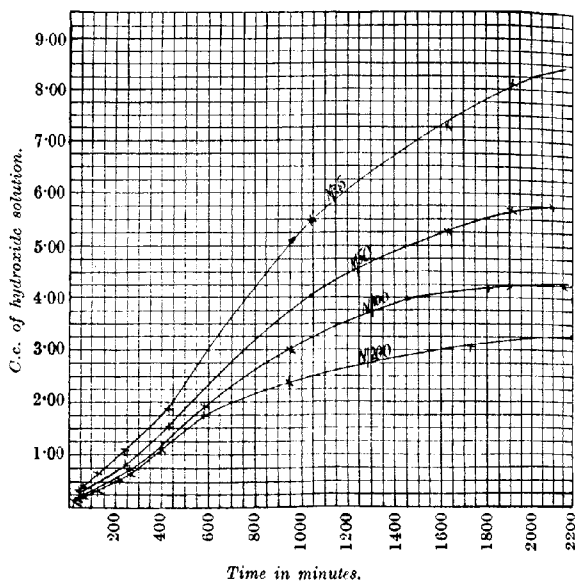
  

<i>N/50-K<sub>2</sub>PtCl<sub>6</sub> Solution.</i>			<i>N/25-K<sub>2</sub>PtCl<sub>6</sub> Solution.</i>		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
40	0.27	0.00105	40	0.32	0.00125
60	0.32	0.00125	60	0.42	0.00164
125	0.51	0.00199	125	0.68	0.00265
240	0.84	0.00328	240	1.10	0.00429
430	1.53	0.00597	430	1.88	0.00733
1035	4.04	0.0158	1035	5.46	0.0213
1630	5.24	0.0204	1630	7.24	0.0282
1910	5.68	0.0222	1910	8.12	0.0317
2050	5.86	0.0229	2280	8.56	0.0334
2400	6.36	0.0248	2600	8.70	0.0339
2700	6.45	0.0252			

These results show that the different solutions reach a condition of equilibrium in almost the same time. The  $N/200$ -solution attains a condition of maximum acidity some two or three hours after the most concentrated one.

If we calculate the percentage of chlorine that has been set free from the platinum salt when equilibrium has been reached, we find that for the four solutions the values are, beginning with the most

FIG. 1.



dilute solution, 74.7, 45.8, 35.2, and 23.2 per cent. of the chlorine present as platonic chloride.

The relationship between the time and the progress of the reaction is better shown by the curves of Fig. 1, where times are plotted as abscissæ against volumes of barium hydroxide solution used for the titration.

The first part of the curve shows nearly a straight line, that is, during the period that the first three-fifths of the reaction is taking place, indicating that the hydrolysis goes on at an almost constant rate for a considerable period of time. A velocity-constant for this part of the reaction may then be calculated by dividing the

amount of hydrogen chloride formed by the time and multiplying by the dilution.

There is an indication in the case of the two weaker solutions of what Goodwin (*Zeitsch. physikal. Chem.*, 1896, **21**, 1) has termed an induction period, during which the reaction proceeds very slowly. This would suggest that some substance may be forming—a product of the reaction—that catalyses the reaction during its later stages. This point can be discussed to better advantage when considering the reaction that takes place in the dark.

In order to show that the rate of the reaction is proportional to the intensity of the light for a given source of light, the following measurements were made for *N*/100- and *N*/200-solutions placed at a distance of 40 cm. from the source. The temperature and other factors were maintained the same as in the previous measurements.

<i>N</i> /200-Solution at 40 cm.		<i>N</i> /100-Solution at 40 cm.	
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.
220	0.14	125	0.16
405	0.28	265	0.24
585	0.48	410	0.40
950	0.76	580	0.64
1741	1.44	955	0.94
2472	2.24	1455	1.68
3195	2.56	1810	2.12
4010	2.70	2370	2.92
5135	2.84	3165	3.48

For the sake of comparison, we may set down opposite the volume of hydroxide solution necessary for the titration the time during which the solution was exposed; the corresponding time for the solutions exposed at 20 cm. distance is also shown in the table, these values being taken from the curves of Fig. 1.

TABLE III.

Ba(OH) <sub>2</sub> solution, c.c.	Time of exposure for solution <i>N</i> /200, minutes.		Ba(CH) <sub>2</sub> solution, c.c.	Time of exposure for solution <i>N</i> /100, minutes.	
	At 20 cm.	At 40 cm.		At 20 cm.	At 40 cm.
0.14	40	220	0.16	35	125
0.28	100	405	0.24	50	265
0.48	188	585	0.40	125	410
0.76	300	950	0.64	205	580
1.44	510	1741	0.94	315	955
2.24	870	2472	1.68	515	1455
2.56	1125	3195	2.12	640	1810
2.70	1280	4010	2.92	925	2370
2.84	1460	5135	3.48	1175	3165
2.92	1555	5665	4.00	1500	4105
			4.16	1860	6685



These results show that at the beginning of the hydrolysis the rate of the reaction is approximately proportional to the intensity of the light. However, after the reaction has proceeded a certain distance—when about one-tenth of the total amount of hydrogen chloride has been formed—the rate of the reaction for the solution at the greater distance is more rapid than the intensity law would predict. This is perhaps to be expected if the later stages of the reaction are influenced by a product formed during the hydrolysis. It is worth noting that this change in rate occurs when practically the same amount of hydrogen chloride has been formed in each solution. The final equilibrium point is apparently not affected by a change in the intensity of the light, as the titration is almost identical in the two cases.

It will be of interest to record at this point the behaviour of solutions of the platinichloride when made up and kept in the dark. The solutions were protected from the light by wrapping the container in black paper and then enclosing it in a thick wooden box, blackened within and without. The following tables will show the results of these observations. In the preparation of the *N*/25-solution the water had been very carefully distilled, and boiled again just before using. The salt had been kept in the dark for several days before making up the solutions, and every precaution was taken to exclude light, both while preparing the solutions and after.

The volumes of solution and weights of hydrogen chloride are expressed in the units used before.

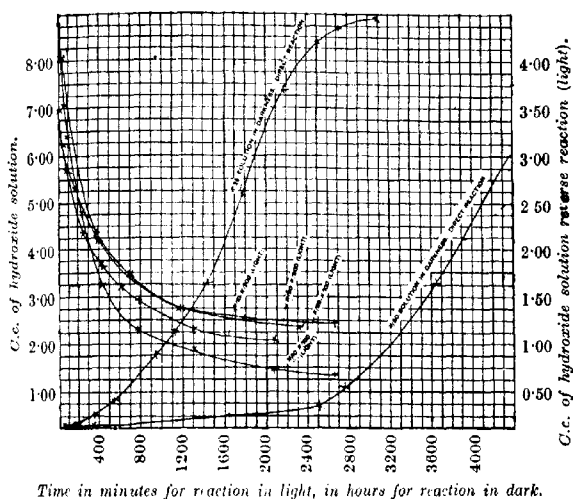
TABLE IV.

<i>N</i> /25-K <sub>2</sub> PtCl <sub>6</sub> in Darkness.			<i>N</i> /50-K <sub>2</sub> PtCl <sub>6</sub> in Darkness.		
Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl Grams.	Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl Gram.
68.3	0.06	0.00023	68.3	0.04	0.00016
162.0	0.12	0.00047	162.0	0.04	0.00016
354.0	0.28	0.00110	354.0	0.04	0.00016
546.0	0.60	0.00236	546.0	0.04	0.00016
937.0	1.52	0.00592	1625.0	0.28	0.00110
1120.0	2.04	0.00796	2455.0	0.44	0.00173
1440.0	3.04	0.01185	2755.0	0.84	0.00330
1775.0	4.94	0.01927	3662.0	1.54	0.01177
2177.0	7.14	0.02785	4850.0	6.04	0.02355
2515.0	8.13	0.0317			
2735.0	8.46	0.0330			
3090.0	8.65	0.0337			

In the case of the *N*/100- and *N*/200-solutions, there was no indication that hydrolysis had even started after they had been in the dark for six months. For the *N*/25- and *N*/50-solutions, the

results were as indicated. In the latter case, the hydrolysis had not proceeded far enough to be measured until approximately thirty days had elapsed. For the  $N/25$ -solution, the reaction had proceeded to such an extent that it could be detected at the end of five days. The curves of Fig. 2, obtained by plotting the results of table IV, show much more distinctly the character of the "induction" period. This period becomes more extended and exaggerated as the solution becomes more dilute, until, for a solution as dilute as  $N/100$ , no hydrolytic decomposition whatever takes place over as extended a period as six months. It appears

FIG. 2.



strange, perhaps, that the more dilute solutions are the more stable. The concentration of the hydrogen and hydroxyl ions has evidently little to do with the progress of the reaction, although it might be argued that these factors are practically constant for the different solutions, the proportion of water to salt being so large for all concentrations studied.

The time required for the  $N/25$ -solution to reach an equilibrium point in darkness is approximately one hundred times as long as when exposed to the radiations of the 300-watt lamp. For the  $N/50$ -solutions, the difference in time is somewhat greater.

It seems possible that for the more concentrated solutions a

sufficient, although perhaps an exceedingly small, amount of some substance—perhaps an hydroxy-salt—is produced when the salt is first dissolved to catalyse the hydrolytic reaction, and, in the case of the  $N/25$ -solution, to give the reaction an appreciable velocity almost at the beginning. The shape of the curves of Fig. 2 is then more easily understood. The steep parts show the accelerating effect of the catalyst, in the absence of any effective radiations, in a very striking way. For the more dilute solutions, this catalyst is not produced in concentrations high enough to affect the progress of the reaction.

#### *The Reverse Reaction.*

On testing the solutions to determine whether the reaction could be driven in the opposite direction, it was found that when potassium chloride, sodium chloride, or hydrochloric acid was added to a hydrolysed solution, the reaction proceeded in the opposite direction, either in the dark or in the light, the extent to which the reverse reaction took place depending, in the case of any one solution, on the amount of chloride that had been added. The rate at which the reverse reaction proceeded was very much slower in the dark than in the light, as measurements given below will show. The effect of platinum-black on the reaction was also studied, as set forth in the tables. For this purpose, a strip of platinum foil was covered electrolytically with platinum-black, and this strip, after being thoroughly washed, was immersed in the solution to be studied.

TABLE V.

Reverse Reactions in Light:  $N/100\text{-K}_2\text{PtCl}_6$  Solution.

$N/10\text{-KCl}$			$N/20\text{-KCl}$		
Time, minutes.	$\text{Ba(OH)}_2$ solution, c.c.	HCl. Gram.	Time, minute.	$\text{Ba(OH)}_2$ solution, c.c.	HCl. Gram.
Initial	4.29	0.0167	Initial	4.29	0.0167
65	3.40	0.0133	20	3.90	0.0152
95	3.08	0.0120	245	2.56	0.00998
255	2.28	0.0089	385	2.06	0.0080
430	1.50	0.0059	700	1.62	0.0063
620	1.16	0.00452	1175	1.26	0.0049
775	1.04	0.00436	1775	1.16	0.0045
1305	0.82	0.00320	2665	1.10	0.0043
2070	0.60	0.00234			
2660	0.56	0.00218			

TABLE V. (*continued*).*N*/200- $K_2PtCl_6$  Solution.

<i>N</i> /10-KCl.			<i>N</i> /20-KCl.		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	3.35	0.0131	Initial	3.35	0.0131
65	2.86	0.0112	35	3.00	0.0117
95	2.74	0.0107	185	2.54	0.0099
255	2.06	0.0080	385	1.98	0.0077
430	1.70	0.0066	810	1.46	0.0057
620	1.48	0.0058	1205	1.24	0.0052
775	1.34	0.0052	1775	1.12	0.0044
1305	1.04	0.00405	2323	1.06	0.0041
2070	0.92	0.00359	4850	0.86	0.00335
4850	0.59	0.00230	5600	0.70	0.00273
5600	0.52	0.00203			

The reverse reaction is seen to take place at a comparatively rapid rate at the beginning, the amount of change being greater here, in a given time, than for the direct reaction. This is no doubt because the added salt has so greatly increased the concentration of the chlorine ion. Towards the end, however, the progress becomes very slow, with the result that the time required for the reverse action to go to completion is much greater than the time necessary for the hydrolysis to take place. In the case of the *N*/200-platinum solutions, the time required for the reverse reaction is much greater than for the *N*/100-solutions.

The latter stage of the reaction for the *N*/100-potassium platinichloride-*N*/10-potassium chloride solution is complicated by the fact that, as the potassium platinichloride is regenerated, the solution becomes supersaturated with respect to this compound, and it crystallises out to a slight extent. This probably explains the crossing of the curves for the *N*/10-potassium chloride solutions, as shown in Fig. 2. This also goes to show that the hydrolysed salt is slightly more soluble in potassium chloride solutions than the normal compound.

If the rate of the reverse reaction is expressed according to the usual formula, using the results of the measurements, say, for the *N*/200-potassium platinichloride-*N*/10-potassium chloride solution, a constant is not obtained. The expression for a unimolecular reaction gives a value which continually diminishes, whilst the bimolecular formula yields a continually increasing number.

The results of measurements made on solutions reacting in the reverse direction in the dark are shown below in table VI. The effect of the addition of sodium chloride to the hydrolysed solution is also shown.

TABLE VI.

*Reverse Reactions in Darkness.**Potassium Chloride Added.*

<i>N</i> /50- $K_2PtCl_6$ . <i>N</i> /20-KCl.			<i>N</i> /200- $K_2PtCl_6$ . <i>N</i> /10-KCl.		
Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	6.60	0.0257	Initial	3.35	0.0131
1.50	5.32	0.0208	4.25	3.22	0.0126
19.58	4.98	0.0194	49.25	2.60	0.0102
73.50	4.32	0.0169	317.0	1.98	0.0077
260.50	3.34	0.0130	1973.0	1.10	0.0043
601.50	2.80	0.0109	3797.0	0.90	0.00351
1101.5	2.38	0.0093	5957.0	0.72	0.00281
1657.0	2.10	0.0082	8693.0	0.52	0.00203
2540.0	1.84	0.0072			
3096.0	1.80	0.0070			

*N*/200- $K_2PtCl_6$ . *N*/20-KCl.

Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	3.35	0.0131
49.25	2.78	0.0108
317.0	2.22	0.0087
1973.0	1.32	0.00515
3797.0	1.12	0.00437
5957.0	0.92	0.00359
8693.0	0.74	0.00289

*Sodium Chloride Added.*

<i>N</i> /200- $K_2PtCl_6$ . <i>N</i> /10-NaCl.			<i>N</i> /200- $K_2PtCl_6$ . <i>N</i> /20-NaCl.		
Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	3.35	0.0131	Initial	3.35	0.0131
48	2.62	0.0102	48	2.94	0.0115
75	2.42	0.0094	76	2.82	0.0110
1732	1.34	0.0052	—	—	—
3556	1.10	0.00429	3556	2.16	0.0084
5716	0.86	0.00335	5716	1.80	0.0070
8452	0.50	0.00195	8452	1.72	0.0067
12300	0.29	0.00109	16828	1.50	0.0059
			20476	1.20	0.0047

*N*/100- $K_2PtCl_6$ . *N*/10-NaCl.

Time, hours.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	4.29	0.0167
29	3.98	0.0155
219	3.42	0.0133
1296	2.52	0.0098
2376	2.16	0.0084
4488	1.68	0.00655

These results show that the reverse reaction, brought about by the addition of a soluble chloride to the hydrolysed solution, continues in the absence of light until, for the more concentrated solutions, much the same equilibrium point is reached as in the case of the same reaction taking place in the light. For the more dilute solutions, the latter equilibrium point is past, the reaction continuing for approximately two years, by which time the hydrolysis has almost disappeared.

The catalytic effect of platinum-black on the reverse reaction is shown by the results set forth below. In the first case, the solutions were exposed to the radiations from the 300-watt lamp, whilst the second series of results refers to the reaction taking place in the absence of light. In each case, these reactions were studied simultaneously with solutions kept under exactly the same conditions, except that no platinum-black was present.

TABLE VII.

*Reverse Reactions with and without Platinum-black.  
In Light.*

$N/100\text{-K}_2\text{PtCl}_6$ .  $N/20\text{-KCl}$ .

With Platinum-black.			Without Platinum-black.	
Time, minutes.	$\text{Ba}(\text{OH})_2$ solution, c.c.	HCl. Gram.	$\text{Ba}(\text{OH})_2$ solution, c.c.	HCl. Gram.
Initial	4.29	0.0167	4.29	0.0167
20	3.90	0.0152	3.90	0.0152
245	2.56	0.0100	2.56	0.0100
385	2.06	0.0080	2.06	0.0080
700	1.62	0.0062	1.62	0.0063
1175	1.26	0.0049	1.26	0.0049
1775	1.16	0.0045	1.16	0.0045
2665	1.10	0.0043	1.10	0.0043

*In Darkness.*

$N/100\text{-K}_2\text{PtCl}_6$ .  $N/20\text{-KCl}$ .

With Platinum-black.			Without Platinum-black.	
Time, hours.	$\text{Ba}(\text{OH})_2$ solution, c.c.	HCl. Gram.	$\text{Ba}(\text{OH})_2$ solution, c.c.	HCl. Gram.
Initial	4.29	0.0167	4.29	0.0167
28.75	3.72	0.0145	3.88	0.0151
219.7	2.84	0.0111	3.52	0.0137
1296.0	1.80	0.0070	2.36	0.0092
2376.0	1.36	0.0053	2.02	0.0079
4488.0	1.14	0.0045	1.54	0.0060
8376.0	1.02	0.0040	1.30	0.0051

It is apparent that the effect of the platinum-black is not great enough to show when the reaction is taking place at a relatively rapid rate before the lamp, but it is quite noticeable when the reaction is proceeding slowly in the dark.

A few results will show the effect of the presence of a neutral salt, such as potassium nitrate, in the solution undergoing hydrolysis. The values from measurements of two solutions are given.

TABLE VIII.

*Direct Reaction with Potassium Nitrate.*

<i>N/200-K<sub>2</sub>PtCl<sub>6</sub>, N/20-KNO<sub>3</sub>.</i>			<i>N/200-K<sub>2</sub>PtCl. N/10-KNO<sub>3</sub>.</i>		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HCl. Gram.
Initial	0.00	—	Initial	0.00	0.0000
100	0.20	0.00078	100	0.22	0.00086
175	0.40	0.00156	190	0.46	0.00179
350	0.78	0.00304	225	0.58	0.00226
465	1.00	0.00390	315	0.84	0.00328
665	1.44	0.00562	605	1.52	0.00592
850	1.86	0.00725	800	1.91	0.00745
1380	2.66	0.0104	1215	2.40	0.00936
1775	2.92	0.0114	1775	2.90	0.0113
2020	3.04	0.0119	2020	3.08	0.0120
2650	3.28	0.0128	2650	3.26	0.0127
3000	3.44	0.0134	3000	3.40	0.0133

These results show that whilst the potassium nitrate has a retarding effect at the beginning of the reaction, the acidity of the solution finally reaches just as high a value as in the absence of the neutral salt. The total time required for the reaction to reach an equilibrium point is but slightly greater when the potassium nitrate is present. In agreement with the retarding effect of the nitrate is the fact that the solution which contains the greater amount of neutral salt lags slightly behind the other.

As stated above, it appears from the results in table I that a substance may be formed from the hydrolysis which acts as a catalyst of the reaction, increasing the speed very perceptibly during the first half of the decomposition. This point was further tested, as follows. Two solutions were prepared in the same manner, of equal concentration as regards platinum salt, whilst one contained 1 c.c. of dilute hydrochloric acid. They were then exposed at the same temperature and at the same time to the radiations from the lamp, at equal distances from the source. Measurements of the acidity of the solutions were then made at frequent intervals. The results failed to show any accelerating influence whatever on the part of the hydrochloric acid. The

reaction necessarily did not proceed so far in the solution containing the added chlorine ions, but this was the only effect noticed.

Another experiment with the same object in view was made, as follows. Two solutions of the platinum salt were prepared, one  $N/100$ , the other  $N/400$ . These were exposed to the light until partly hydrolysed, then placed in the dark. The acidity of the more concentrated solution was measured after twenty days, and the measurement showed that the hydrolytic reaction had continued until the usual equilibrium point had been reached. In the case of the  $N/400$ -solution, a measurement was made after thirty days, but the rise in acidity, if any, was so small that it could not be detected with certainty. After thirty-eight days more, the result of another measurement indicated that the hydrolysis was proceeding, but very slowly. A 10 c.c. portion, which neutralised 0.88 c.c. of alkaline solution when first placed in the dark, now required 0.98 c.c. The next two months brought no perceptible change in this solution, and sixteen months after it had been placed in the dark a 10 c.c. portion required only 1.10 c.c. of hydroxide solution. Another  $N/400$ -solution, made up at the same time as this one, but never exposed to the light, showed no indication of any hydrolytic action after sixteen months. It would seem as if a certain concentration of the catalytic reagent was necessary before the hydrolysis will proceed. In the case of the  $N/400$ -solution that had been exposed to the light, this concentration had apparently just been reached before the solution was placed in the dark.

It was not expected that the accelerating influence of platinum-black would be sufficiently great to be noticed in a solution undergoing hydrolysis before the light. It was thought worth while, however, to measure this effect on solutions reacting in the dark. Accordingly, two solutions were carefully prepared, each  $N/25$ . In one was placed 0.05 gram of platinum-black. Both solutions were placed in the dark and measured from day to day. After three days, 10 c.c. of one solution neutralised 0.06 of alkali solution, whilst the same volume of the one containing the platinum-black required 0.25 c.c. After five days, the corresponding volumes of alkali solution were 0.06 c.c. and 0.45 c.c. The effect of the platinum-black was very evident both in starting the hydrolysis and in accelerating the reaction.

Another experiment, almost identical with this one, was made by adding 5 c.c. of an  $N/25$ -solution completely hydrolysed to a newly prepared  $N/100$ -solution, and placing this in the dark. The reading for a 10 c.c. portion of this solution was now 0.98 c.c. of alkali; after two months, the volume of alkali required for a 10 c.c. portion was 2.32 c.c., showing that a sufficient amount of



the accelerating substance had been added to cause the hydrolysis to take place.

The effect of the temperature on the rate of the reaction and the extent of the hydrolysis received some attention. It was first ascertained whether a solution which would not undergo hydrolysis in the dark at the ordinary temperature would hydrolyse if kept at 80°. An  $N/100$ -solution was tested in this way. The titration for a 10 c.c. portion of this solution was 0.04 c.c. at 20°. After being kept in the dark at 80° for three hours, the corresponding titration was 0.16 c.c. On cooling to 20°, still in the dark, the titration fell to 0.08 c.c. After being kept in the dark at 80° for another period of three hours, a 10.0 c.c. portion again required 0.16 c.c. of alkali. In the absence of light, the temperature has little, if any, influence on the hydrolysis. The same conclusion is drawn from a comparison of the rate of the reaction taking place at 25° with that at 35°. The variation here is only manifest toward the end of the reaction, when the difference in the equilibrium point—a greater degree of hydrolysis at the higher temperature—is sufficient to show in the final readings.

For the purpose of ascertaining to what extent the hydrolysis would be increased by a rise in temperature, three solutions were exposed to the radiations of the 300-watt lamp at a distance of 20 cm., the water-bath being maintained at the temperature shown below. From time to time, 10 c.c. portions of the platinum solutions were withdrawn and titrated, the light being continued at any one temperature until equilibrium had been attained.

TABLE IX.

*Effect of Temperature on the Hydrolysis.*

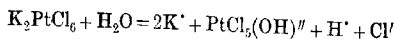
Temperature.	$N/100\text{-K}_2\text{PtCl}_6$ .		$N/50\text{-K}_2\text{PtCl}_6$ .		$N/25\text{-K}_2\text{PtCl}_6$ .	
	Ba(OH) <sub>2</sub> solution, c.c.	HCl (100 c.c.), Gram.	Ba(OH) <sub>2</sub> solution, (100 c.c.), c.c.	HCl (100 c.c.), Gram.	Ba(OH) <sub>2</sub> solution, c.c.	HCl (100 c.c.), Gram.
20°	4.29	+0.0167	6.45	+0.0252	8.70	+0.0339
50	5.24	+0.0204	7.45	+0.0291	10.16	+0.0396
80	5.90	+0.0230	8.20	+0.0319	11.06	+0.0431

If we express the increase in the acidity of these solutions as percentages of the values at 20° we obtain the following coefficients for temperatures between 20° and 80°:  $N/100$  0.62,  $N/50$  0.45,  $N/25$  0.45 per cent.

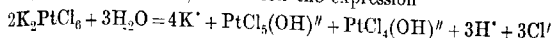
These coefficients are not very different for the several concentrations studied. From the amount of hydrogen chloride formed at 80°, we find that for the  $N/100$ -solution 63 per cent. of the

chlorine present as platonic chloride has been used to form hydrogen chloride.

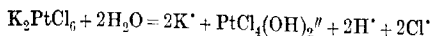
If we represent by chemical equations the several stages of the hydrolytic decomposition of the platinum salt, we find that for the *N*/25-solution the equation



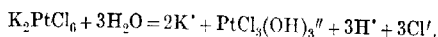
indicates pretty closely the extent to which the hydrolysis has taken place, whilst for the *N*/50-solution the expression



would represent more nearly the condition of the solution. When the solutions are as dilute as *N*/100 or *N*/200, the respective equations would be



and



The above equations correspond with a temperature of 20°. At higher temperatures, the decomposition of the salt is more nearly complete, which is in agreement with the fact that when a dilute solution of the platinichloride is boiled in the light, an insoluble substance is deposited.

Obviously the possibilities of this hydrolytic action should be kept in mind when making a determination of potassium by means of this salt; if a solution of the platinichloride is being evaporated, a sufficient amount of hydrochloric acid must be present to prevent the hydrolysis taking place, whilst if the salt is being precipitated, hydrochloric acid must again be present to ensure the formation of the normal compound.

Potassium platinibromide shows some interesting features not noticeable in the case of the platinichloride, and it is hoped to submit soon a communication dealing with this compound.

#### *Summary.*

It has been shown that solutions of potassium platinichloride undergo hydrolysis when exposed to the action of light.

If the solution is as concentrated as *N*/50, this hydrolysis will begin and will be completed in the dark; for a *N*/100-solution or one more dilute, no decomposition takes place when light is excluded.

A substance is formed by the hydrolysis which catalyses the reaction, and will initiate the decomposition in a newly prepared solution.

The addition of a soluble chloride to the hydrolysed solution

causes a complete reversal of the reaction, showing that the substances formed during the direct reaction are soluble.

The reverse reaction is influenced by light in much the same way as the direct. The complete reversal of a solution as dilute as  $N/200$  requires nearly two years.

A neutral salt has a slight retarding effect on the direct reaction, but does not influence the equilibrium point.

The accelerating influence of platinum-black on both the direct and reverse reactions is quite noticeable when these reactions are taking place in the dark, but is not measurable when light is acting on the solutions.

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[Received, July 23rd, 1920.]

## CXXVI.—*Studies in Catalysis. Part XIV. The Mechanism of the Inversion of Sucrose.*

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In connexion with the investigations carried out in this laboratory on the chemical reactivity of molecular and ionic species from the point of view of the radiation hypothesis, it was found necessary, in one section of the work, to make a series of determinations of velocity-constants in the case of a few familiar reactions, such as the inversion of sucrose, with the object of studying more particularly the influence of change of environment on the rate of the reaction. The principle of mass action, in its usual formulation, affords no information of an a priori kind regarding the effect of environment. It is hoped that the radiation hypothesis may be of assistance in this connexion (compare Lewis, *Scientia*, 1919, 25). As a preliminary, it is necessary to possess as clear a view as possible of the actual material mechanism of the selected reaction in order to be able to proceed with some degree of confidence to the further problems involved in alterations of material and temperature environment. The inversion of sucrose is a reaction particularly suitable for the purpose in view in so far as precision of measurement is concerned. Further, this reaction has been frequently investigated, but, in spite of this, the inversion process

obviously requires further investigation, more particularly as regards the way in which the hydrogen ion enters into the process.

The present research was undertaken primarily for this purpose. As will be seen, the experimental measurements consist on the one hand of determinations of reaction velocities, and on the other of determinations of the average (geometric mean) activities of the hydrogen ions, obtained by the electrometric method. In agreement with the conclusion already reached by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) in connexion with other reactions catalysed by ions, it has been found that the activity of the hydrogen ion, as defined by G. N. Lewis, is the determining factor for the rate of the reaction. This conclusion is of great importance, as it not only includes to a certain extent the phenomenon known as the solvent displacement effect, but also, as pointed out by Harned, appears to exclude the necessity of ascribing any catalytic influence to the undissociated molecule of the acid. In order to obtain data which could be employed for various kinds of calculation, care has been taken to determine the amounts of all constituents, water included, in known volumes of the various solutions.

As will be shown later, the most probable material mechanism of the inversion reaction is that expressed by  $\text{RH}^+ + \text{H}_2\text{O} \rightarrow \text{dextrose} + \text{lævulose}$ . That is, the reaction is a true bimolecular one, between a molecule of water and a complex ion, formed by the addition of hydrogen ion to the sucrose molecule.

#### EXPERIMENTAL.

##### *Reaction Velocity Measurements.*

The rate of inversion of sucrose was carried out in the ordinary manner with the usual precautions at 20°, 30°, 40°, and 50° in the presence of *N*/10-sulphuric acid, the initial concentration of sucrose being varied over a wide range, namely, from 10 to 70 per cent., in order to bring into prominence any effect produced by the displacement of the solvent, water, the volume of the various solutions being maintained constant. All determinations were carried out in duplicate, and satisfactory unimolecular velocity-constants were obtained throughout the entire range examined. To save space, the mean values only of the observed velocity-constants, referred to the base *c* and in seconds<sup>-1</sup>, as well as the initial concentrations of sucrose and water, are given in the following table.

TABLE I.

Catalyst: 0.1N-H<sub>2</sub>SO<sub>4</sub>.

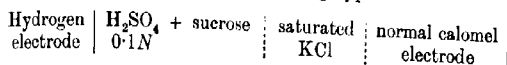
Grams of sucrose in 100 c.c. of solution.	Gram- molecules of water ( $M=18$ ) per litre.	Unimolecular velocity-constant.			
		$\times 10^6$ at 20°.	$\times 10^6$ at 30°.	$\times 10^6$ at 40°.	$\times 10^4$ at 50°.
10	51.95	4.43	1.83	6.73	2.29
20	48.45	4.79	1.97	7.37	2.55
30	44.99	5.21	2.12	8.04	2.81
40	41.62	5.54	2.29	8.80	3.08
50	38.09	5.95	2.45	9.53	—
60	34.59	6.22	2.58	10.22	—
70	30.94	6.29	2.66	10.92	3.94

It will be observed that in all cases displacement of the water by the sucrose causes a definite increase in the velocity-constant, a further illustration of the anti-catalytic effect of water already observed in other reactions, for example, hydrolysis of esters. If the reaction is a true bimolecular one, it is necessary to divide the velocity-constants by the corresponding concentration of water in order to obtain comparable quantities in so far as this stoichiometric correction is concerned. Whether the observed velocity-constants require to be thus divided or not, it is possible to obtain values for the critical increment,  $E$ , by means of the equation  $d \log k / dT = E / RT^2$ , from the velocity-constants at different temperatures. It was thus found that with an increasing initial concentration of sucrose, the value of  $E$  rises steadily over all three ranges of temperature investigated, namely, 20° to 30°, 30° to 40°, and 40° to 50°. That is, the critical increment (or the temperature-coefficient) apparently rises, whilst the velocity-constant itself also increases. As this is in direct contradiction to the conclusion already drawn, namely, that the greater the critical increment the smaller, *ceteris paribus*, the velocity-constant, it was concluded that the catalytic conditions were not comparable at any pair of temperatures, as the content of sucrose was varied. The behaviour, in fact, could be accounted for on the assumptions that (a) the catalytic influence of the acid at any given temperature increases with increasing concentration of sucrose, and (b) that this increase in catalytic activity is greater the higher the temperature. This conclusion did not appear to be a very probable one on the basis of the degree of electrolytic dissociation of the acid, for in the case of sulphuric acid the catalytic effect ascribed to the undissociated molecule is approximately the same as that of the hydrogen ion, and in general the ratio of the catalytic effect ascribed to the molecule to that of the ion decreases as the temperature increases. Owing to the large viscosity effects produced by a variation in the

concentration of sucrose, electrical conductivity measurements could not give direct information, even assuming that the original equation of Arrhenius was valid, an assumption which has recently been called in question. On this account, it was decided to determine the activity or thermodynamic concentration of the hydrogen ions (strictly speaking, the geometric mean of the activity of hydron and  $\text{HSO}_4'$ ) by means of electromotive-force measurements.

*Activity of Hydrogen Ion in Aqueous Solutions of Sucrose.*

The cell employed was of the following type:



The use of a saturated solution of potassium chloride as a middle liquid, to eliminate contact potential differences, has been frequently recommended (compare Fales and Vosburgh, *J. Amer. Chem. Soc.*, 1918, **40**, 1291). The absolute value of the normal calomel electrode was taken to be +0.56 volt at 18°. Using T. W. Richards' value for the temperature-coefficient of this electrode, namely, 0.0006 volt per degree, the potential difference of the calomel electrode at 20° was taken to be 0.5612 volt, at 40° 0.5732 volt. The value of  $\pi_{\text{H}}$ , the potential of the hydrogen electrode in the sulphuric acid-sucrose solutions, was obtained by means of the following equations:

$$\pi_{\text{H}} = 0.277 + 0.058 \log_{10} \text{H}^+ \text{ at } 20^\circ$$

and

$$\pi_{\text{H}} = 0.296 + 0.062 \log_{10} \text{H}^+ \text{ at } 40^\circ,$$

where the electrolytic potential of hydrogen has been assumed to vary directly as the absolute temperature. The absolute value may not be correct on this basis, but as the quantity involved is a constant at any given temperature, the relative values of  $\pi_{\text{H}}$  at two different temperatures are comparable.

Table II contains the *E.M.F.* data obtained at 20°, the last column giving the average activity of the hydrogen ion expressed in gram-molecules per litre. Table III contains similar data for 40°. In all cases, dissolved oxygen was removed from the sucrose solutions to prevent any change in the sucrose in contact with the platinised platinum electrode.

TABLE II.

*Temperature, 20°. 0.1N-H<sub>2</sub>SO<sub>4</sub>.*

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of sucrose per litre.	Gram-molecules of water ( $M = 18$ ) per litre.	E.M.F. of cell observed, in volts.	P.d. of hydrogen electrode, $\pi_H$ .	Activity of hydrogen ion in gram-molecules per litre.
0	0	55.55	0.3555	0.2057	0.060
10	0.292	51.95	0.3520	0.2092	0.068
20	0.585	48.45	0.3485	0.2127	0.078
30	0.877	44.99	0.3450	0.2170	0.0895
40	1.169	41.62	0.3410	0.2202	0.105
50	1.460	38.09	0.3380	0.2282	0.118
60	1.755	34.59	0.3345	0.2267	0.139
70	2.047	30.94	0.3313	0.2299	0.162

TABLE III.

*Temperature, 40°. 0.1N-H<sub>2</sub>SO<sub>4</sub>.*

Grams of sucrose in 100 c.c. of solution.	E.M.F. of cell, in volts.	P.d. of hydrogen electrode.	Activity of H' in gram-molecules per litre.
0	0.3580	0.2152	0.050
10	0.3545	0.2187	0.056
20	0.3522	0.2210	0.062
30	0.3460	0.2272	0.078
40	—	—	0.091*
50	0.3370	0.2362	0.109
60	—	—	0.130*
70	0.3280	0.2452	0.152

(Values marked with an asterisk are interpolated from the curve.)

It will be observed that the activity of the hydrogen ion is less at 40° than it is at 20°. This would be expected for the *concentration* of the ion, since the dissociation of the acid is accompanied by an evolution of heat.

The first conclusion to be drawn from the above data is that the activity of the hydrogen ion increases appreciably at both temperatures with an increase in the concentration of the sucrose, and further, as shown later in the figure, the rate of increase in activity is greater at 40° than it is at 20°. The bearing of these results on the velocity-constants will be considered in the next section.

The second conclusion is that the activity of an ion is related to its concentration in a very secondary manner. This has already been shown to be the case by several American investigators. The effect is well marked in the present instance. Thus, when the sucrose content is 70 per cent., the thermodynamic concentration of the hydrogen ion is 0.162 at 20° and 0.152 at 40°, although the

maximum actual concentration of hydrogen ion cannot exceed 0.10.

The third conclusion is that the displacement of the solvent by a non-electrolyte, sucrose, produces effects entirely analogous to those produced by addition of neutral salts, the addition of the sucrose, and consequent elimination of water, causing an increase in the activity of hydrogen ion from two- to three-fold. It is proposed to investigate this aspect of the displacement effect (compare Griffith and Lewis, T., 1916, 109, 67) in further researches in this laboratory. The activity of ions in presence of a non-electrolyte appears to have been investigated in a single instance only, namely, by Harned (*J. Amer. Chem. Soc.*, 1915, 37, 2467), who determined the activity of the hydrogen ion from hydrochloric acid, in the presence of mannitol, without observing, however, any marked effect over the concentration range employed.

#### THE PROBABLE MECHANISM OF THE INVERSION PROCESS.

It was found that the directly observed velocity-constants (table I) at 20°, when divided by the concentration of the water and also by the corresponding activity of the hydrogen ion, gave a quantity which was a constant within the limit of the experimental error. Similarly, the data at 40° gave a constant independent of the sucrose or water content, the numerical value being, of course, greater than that at 20°. These constants represent bimolecular velocity-constants reduced to unit activity of hydrogen ions. The values are given in tables IV and V.

TABLE IV.

Temperature, 20°. 0.1N-H<sub>2</sub>SO<sub>4</sub>.

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of water (M=18) per litre.	Unimolecular velocity-constant observed. $\times 10^4$ .	Unimolecular velocity-constant divided by water concentration. $\times 10^4$ .	Unimolecular velocity-constant $\times 10^4$ divided by water and also by activity of H <sup>+</sup> ions.
0	55.55	4.14*	7.46*	1.24
10	51.95	4.43	8.53	1.25
20	48.45	4.79	9.88	1.27
30	44.99	5.21	11.58	1.29
40	41.62	5.54	13.31	1.27
50	38.09	5.95	15.61	1.32
60	34.59	6.22	17.97	1.29
70	30.94	6.29	20.33	1.25

Mean =  $1.27 \times 10^{-4}$ .

(Values marked with an asterisk are obtained by extrapolation.)



TABLE V.  
*Temperature, 40°. 0.1N-H<sub>2</sub>SO<sub>4</sub>.*

Grams of sucrose in 100 c.c. of solution.	Gram- molecules of water per litre.	Unimolecular velocity- constant observed. $\times 10^5$ .	Unimolecular velocity- constant divided by water concentration. $\times 10^5$ .	Unimolecular velocity- constant divided by water and also by H' activity. $\times 10^5$ .
0	55.55	5.98*	1.08*	2.16
10	51.95	6.73	1.30	2.31
20	48.45	7.37	1.52	2.46?
30	44.99	8.04	1.79	2.30
40	41.62	8.80	2.11	2.31
50	38.09	9.53	2.50	2.30
60	34.59	10.22	2.96	2.27
70	30.94	10.92	3.53	2.33

Mean =  $2.305 \times 10^{-5}$ .

(Values marked with an asterisk are obtained by extrapolation.)

The two mean values,  $1.27 \times 10^{-6}$  at  $20^\circ$  and  $2.305 \times 10^{-5}$  at  $40^\circ$ , represent the true bimolecular velocity-constant,  $k_{11}$ , of the reaction, where  $k_{11}$  is defined by

$$k_{11} = k_{\text{obs}} / [\text{H}_2\text{O}][\text{H}'],$$

where  $k_{\text{obs}}$  is the observed unimolecular velocity-constant,  $[\text{H}_2\text{O}]$  the concentration of the water ( $M=18$ ), and  $[\text{H}']$  is the activity of the hydrogen ion. The values of  $k_{11}$  as thus defined are independent of the concentration of sucrose or water, and also of the activity of the acid catalyst. The values of  $k_{11}$  depend only on the temperature.

Since the change in the observed velocity-constant with the composition of the solution is entirely accounted for, after the introduction of the necessary stoichiometric correction for water, by the activity of the hydrogen ion, it follows that the undissociated molecule of the acid possesses no catalytic effect in this case. This conclusion has already been drawn by Harned (*loc. cit.*) in other cases in the presence of neutral salts. It is hoped that further investigation with other acids will settle the question as to whether this conclusion is a general one for aqueous solutions. In the case of gaseous systems, catalysis by means of acid is scarcely known. De Hemptinne (*Zeitsch. physikal. Chem.*, 1892, **13**, 561) states that a positive catalytic effect is produced by hydrogen chloride gas in the hydrolysis of gaseous esters. In these circumstances, and probably therefore in non-ionising solvents, the undissociated molecule of the acid is the catalysing individual.

The fact that constant values for  $k_{11}$ , as defined above, are

obtained at a given temperature, removes the difficulty already mentioned in connexion with the apparent variation of the critical increment with composition of the system. When the catalytic conditions are really made the same at two different temperatures, a single value for  $E$ , the critical increment per gram-molecule of sucrose inverted, is obtained, this value being independent of the concentration of sucrose or water in the system. The value of  $E$  calculated from  $k_{14}$  at  $20^\circ$  and  $40^\circ$  is 26,390 calories. The accuracy of this value depends on the relative accuracy with which the activities of the hydrogen ions at  $20^\circ$  and  $40^\circ$  have been determined. This numerical value represents the sum of the critical increments of the reactants, which will be shown later to be the complex ion (sucrose  $H^+$ ) and water.

The constancy of  $k_{14}$  may be employed as a criterion in attempting to determine the mechanism of the inversion process by means of stoichiometric equations, for these equations must be such as to lead finally to an expression of the form

$$k_{14} = k_{\text{int}} / [H_2O] [H^+].$$

Apart from this consideration, many alternative modes of expressing the inversion process suggest themselves. We shall consider five of the most probable of these, and show that only one of them is in agreement with the criterion. The latitude of choice arises from the doubt as to whether (a) the hydrogen ion which reacts is hydrated or not, (b) whether the sucrose which reacts is hydrated or not. The problem of hydration is one of the least satisfactory aspects of the theory of solutions, the evidence in most cases being conflicting.

*Possibility 1.*—Assume that practically all the sucrose is hydrated and that the same is true for the hydrogen ions, but that it is the non-hydrated sucrose which reacts with a hydrated hydrogen ion ( $H_2O, H^+$ ). Applying the law of mass action to the hydration of the sucrose,  $R + H_2O \rightleftharpoons (R, H_2O)$ , we have  $K = [R, H_2O] / [R] [H_2O]$ , where  $K$  is the equilibrium constant of hydration and  $R$  stands for non-hydrated sucrose. The inversion process assumed to be correct is  $R + (H_2O, H^+) \rightarrow \text{dextrose} + \text{levulose}$ . Hence, rate of inversion =  $k_{14} [R] [H_2O, H^+]$ . But rate of inversion =  $k_{\text{int, observed}} [(R, H_2O)]$ , since practically all the sucrose has been assumed to be hydrated. Hence,

$$k_{14} = k_{\text{int}} [(R, H_2O)] / [R] [H_2O, H^+] = k_{\text{int}} \cdot K \cdot [H_2O] / [H_2O, H^+].$$

This mechanism requires, therefore, that the product of the observed velocity-constant by the water concentration divided by the activity of the hydrogen ions should be a constant independent of the initial concentration of sucrose. This differs from the true

criterion, and, in fact, the right-hand side of the equation is not a constant. Hence, possibility 1 is incorrect.

*Possibility 2.*—Assume that practically all the sucrose is hydrated, but that the hydrogen ion is practically all unhydrated, and that the inversion process is  $(R, H_2O) + H' \rightarrow \text{dextrose} + \text{lævulose}$ . This leads finally to the conclusion that

$$k_{in} = k_{uni} / [H'].$$

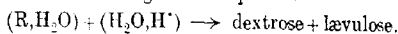
The right-hand side of this expression is not constant. Hence possibility 2 is incorrect.

*Possibility 3.*—Assume that practically all the sucrose is hydrated and that the hydrogen ion is also practically all hydrated, but that it is the non-hydrated hydrogen ion which reacts with hydrated sucrose, as in possibility 2. We have now to allow for  $K_i$ , the equilibrium constant of hydration of the ions,

$$K_i = [H_2O, H'] / [H'] [H_2O].$$

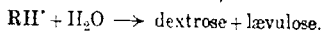
This assumption leads finally to  $k_{in} = k_{uni} \cdot \gamma [H_2O] \cdot K_i / [H_2O, H]$ , which is indistinguishable from possibility 1, and is therefore incorrect.

*Possibility 4.*—Assume that the sucrose and the hydrogen ions are practically all hydrated, and that it is the hydrated form of each which reacts according to the equation



Then,  $k_{in} = k_{uni} / [H_2O, H']$ , which, being equivalent to possibility 2, is incorrect.

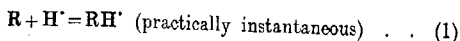
*Possibility 5.*—Assume that the sucrose as well as the hydrogen ions is practically all non-hydrated, and that the first stage is addition to form a complex ion, thus:  $R + H' = RH'$ , which is followed by the true inversion reaction,



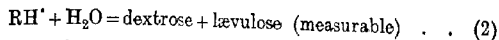
We then have, rate of inversion  $= k_{in}^1 [R]$ , also, rate of inversion  $= k_{in} \cdot [RH'] [H_2O]$ , whence  $k_{in} = k_{uni} [R] / [RH'] [H_2O]$ . Now,  $K_c$ , the equilibrium constant of the complex-ion formation, is given by  $K_c = [RH'] / [R] [H']$ , whence  $k_{in} = k_{uni} / K_c \cdot [H_2O] [H']$ . This is in agreement with the criterion, the right-hand side being a constant, since it only differs from the criterion in containing the constant,  $K_c$ . It may be shown, further, that if the above mechanism is assumed, with the modification that the sucrose is nearly all hydrated, an expression is obtained which is not in agreement with the experimental result. Also, if possibility 5 is employed, with the modification that the ions are practically all hydrated, an equally incorrect expression is obtained. Finally, if possibility 5 is employed, with the modification that both sucrose and the ions are practically all hydrated, an incorrect expression is obtained.

It is reasonable to conclude, therefore, that possibility 5 as it stands is the only satisfactory mechanism.

The two stoichiometric equations which express the inversion process are therefore:



and



It is obvious that this mechanism accounts for the fact that the hydrogen ion is necessary in order that inversion may proceed with measurable speed. There is also some evidence of a preliminary nature for the existence of an addition complex of sucrose and hydrogen ion, which it is hoped may be communicated in detail later.

The mechanism of the inversion process to which we have been led involves equations (1) and (2), and also the assumption that the hydrogen ions and the sucrose molecules are not appreciably hydrated in aqueous solution. This represents the simplest set of conditions, but the result is somewhat surprising. Sucrose is usually regarded as being heavily hydrated in solution. As already pointed out, however, such an assumption would not lead to the observed constancy of the quantity expressed in the final columns of tables IV and V.

#### *Hydrogen-ion Activity as a Function of the Composition of the Solution.*

Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173) has suggested that the catalytic effect of a solvent may be expressed as an exponential function of the concentration of the solvent. A similar relation has been employed by Wilson (*ibid.*, 1920, **42**, 715) to account for the effect of neutral salts on the hydrogen ion, as determined by electrometric measurements. Wilson appears to regard the increase in concentration of the hydrogen ion in the presence of neutral salts as real. The effect, however, involves the activity, and not necessarily the concentration, of the ion. The analogy of the effect produced by the displacement of water by addition of sucrose to that produced by a neutral salt has already been mentioned.

In the conditions obtaining in the present investigation we deal with the simultaneous influence of sucrose and water, since by addition of one constituent a certain amount of the other is eliminated. Let us suppose that the activity of the hydrogen ion can be expressed by

$$[H^+] = A \cdot e^{(aR + bW)} \quad (3)$$

where  $R$  and  $W$  are the concentrations of sucrose and water respectively in gram-molecules per litre,  $b$  and  $b'$  are the catalytic environmental constants characteristic of sucrose and water,  $b$  is a positive, whilst  $b'$  is a negative, quantity.

When there is no sucrose present,  $W$  becomes  $W_0$  (namely, 55.55 gram-molecules per litre) and  $H'$  becomes  $H'_0$ . We can thus re-write equation (3) in the form:

$$H' = H'_0 e^{bR - b'(W_0 - W)} \quad (3a)$$

Hence,

$$\log_e H' = \log_e H'_0 + bR - b'(W_0 - W) \quad (4)$$

In the present case it happens that a straight line is obtained when the concentration of sucrose is plotted against the concentration of the water. Hence we can write  $W = W_0 + pR$ , where  $p$  is a negative constant having the value  $-12.1$ , the sucrose and water being expressed in gram-molecules per litre. Equation (4) can therefore be written in the present case in the form

$$\log_e H' = \log_e H'_0 + (b + b'p)R \quad (5)$$

or, alternatively,

$$\log_e H' = \log_e H'_0 + (b/p + b')(W - W_0) \quad (6)$$

Equations (5) and (6) are both linear, that is, they represent the observed behaviour of the activity of the hydrogen ion as a function of the composition of the mixture, as is shown in the figure (graphs *C* and *D*).

Hence equation (3) is justified in so far, at least, as it satisfies the above condition in the present case. From the experimental data the following mean values are obtained:

$$b - 12.1b' = 0.47 \text{ at } 20^\circ,$$

$$b - 12.1b' = 0.56 \text{ „ } 40^\circ.$$

It will be observed that equations (5) and (6), being equivalent, do not permit of a calculation of  $b$  and  $b'$  separately. Further experimental data involving a different functional relationship between the concentration of the sucrose and the water are required.

In equations (3) to (6) we have employed the most general type of formula in which a possible catalytic effect has even been ascribed to the reactant solute, sucrose. In this connexion, there is an important consideration which has to be taken into account.

The observed unimolecular velocity-constants obtained at various temperatures are found to remain constant, within the limit of experimental error, throughout the entire course of the reaction. This is the case even when the initial concentration of sucrose is as high as 70 per cent., as is shown by the following results of duplicate experiments, which give the observed velocity-constants

obtained with 70 per cent. sucrose at 40° in the presence of  $N/10$ -sulphuric acid. The velocity-constant is calculated to the base  $e$ .

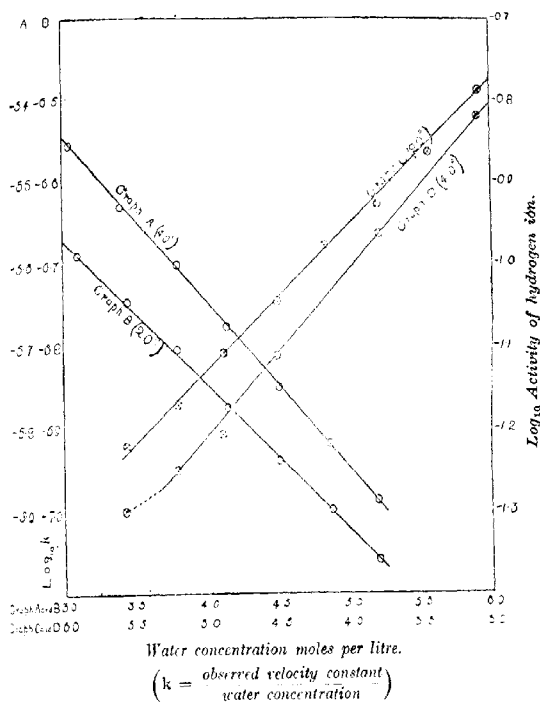


TABLE VI.

Experiment 1.		Experiment 2.	
Time in seconds.	Unimolecular velocity constant $\times 10^3$ .	Time in seconds.	Unimolecular velocity constant $\times 10^3$ .
0	—	0	—
780	10.82	1200	10.81
1500	11.03	1950	10.81
2100	10.98	2460	10.83
3060	11.00	3060	10.77
3900	11.03	3960	10.89
5160	11.07	4440	10.86
6420	11.11	6360	10.96
7500	10.98	6900	10.97
(55 per cent. of the sucrose decomposed.)		(53 per cent. of the sucrose decomposed.)	

The fact that the velocity-constant does not alter indicates that the activity of the hydrogen ion is likewise sensibly constant. As, however, the concentration of the sucrose has diminished by more than one half, it follows that the environmental influence of the sucrose, if any, as measured by the quantity  $b$ , must be the same as that of the dextrose and laevulose formed as a result of the inversion. If these substances are inert, it would follow that  $b=0$ , and that therefore the environmental catalytic term  $b'$ , characteristic of water, is  $-0.039$  at  $20^\circ$  and  $-0.046$  at  $40^\circ$ . The negative value indicates, of course, that the water is a negative catalyst for the process. The question of the absolute value of  $b$  will be dealt with in a later communication.

Returning to the graphs shown in the figure, it will be observed that with diminution in the concentration of water the curves for the hydrogen-ion activity at  $20^\circ$  and  $40^\circ$  are not parallel, but convergent. The same relation is exhibited by the curves for the velocity-constant shown in the same diagram, graphs *A* and *B*.

When the two sets of curves are combined, constant values for  $k_{\text{obs}}$  as defined in the preceding section, are obtained. The relative positions of the two sets of curves afford the most direct evidence yet obtained for the conclusion that the activity of the ion completely determines the velocity of the reaction.

#### *Summary.*

(1) The velocity of inversion of sucrose in the presence of  $N/10$  sulphuric acid has been determined at  $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ , and  $50^\circ$ , the composition of the solution being altered by gradual displacement of the water by the sucrose. The velocity-constants vary with the initial composition of the mixture.

(2) The average activities of the hydrogen ion have been determined electrometrically in the various mixtures referred to in (1) at  $20^\circ$  and  $40^\circ$ . It is shown that the alteration in the velocity-constant can be accounted for completely by (a) allowing for the stoichiometric correction for the water present, and (b) by allowing for the change in the activity of the hydrogen ions.

(3) In agreement with (2), the inversion process is shown to be bimolecular. It consists of two processes, (i) union of the non-hydrated hydrogen ion with a non-hydrated molecule of sucrose, thus,  $R + H^+ = RH^+$ , this process being practically instantaneous, and (ii) the actual inversion reaction,  $RH^+ + H_2O = \text{dextrose} + \text{laevulose}$ . It is also concluded that the hydrogen ions and the sucrose molecules are not sensibly hydrated in aqueous solution.

(4) In agreement with Rosanoff's suggestion regarding the mode

of expressing the influence of solvent catalysts, the activity of the hydrogen ion is found to be an exponential function of the concentration of sucrose and water present.

(5) It is shown that the environmental catalytic influence of a molecule of sucrose, referred to in (4), is identical in magnitude with that exerted by one molecule of dextrose together with one molecule of levulose.

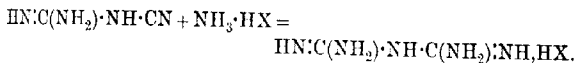
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UNIVERSITY OF LIVERPOOL. [Received, August 4th, 1920.]

### CXXVII.—*The Preparation of Guanidine by the Interaction of Dicyanodiamide and Ammonium Thiocyanate.*

By EMIL ALPHONSE WERNER and JAMES BELL.

By heating a mixture of dicyanodiamide and ammonium chloride at 195° for ten minutes, Bamberger and Dieckmann (*Ber.*, 1892, 25, 545) obtained diguanide,  $C_2H_4N_4$ . The yield was poor, and Ostrogovich (*Bul. Soc. Ştiinţe Bucureşti* 1910, 19, 641), using ammonium iodide in place of the chloride, under similar conditions, obtained a much better result.

The reaction has been represented thus:



The dicyanodiamide complex is supposed to remain intact, whilst the cyanogen group unites with ammonia. On this assumption, the reaction is considered to uphold the cyanoguanidine formula for dicyanodiamide proposed by Bamberger (*Ber.*, 1883, 16, 1459).

In the static condition, dicyanodiamide is stable up to 205°, when it melts, and is simultaneously depolymerised to cyanamide\* and largely repolymerised to melamine (compare Werner, T., 1915, 107, 715).

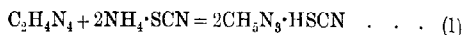
Several experiments have shown that dicyanodiamide is readily depolymerised to cyanamide at comparatively low temperatures in the presence of certain reagents, and its behaviour in the presence

\* This fact is not referred to in the literature: if a gram or two of dicyanodiamide is heated to the melting point in a porcelain crucible and quickly covered with a glass bell-jar standing over a layer of water, the latter after a few moments will be found to give quite a copious yellow precipitate of silver cyanamide on addition of ammonio-silver nitrate solution.



of ammonium thiocyanate, for example, furnishes a case in point which is of practical value.

Pure guanidine thiocyanate has been easily prepared, in accordance with the equation



Whilst the main change is equal to 90 per cent. of the theoretical, it is accompanied by a secondary reaction, whereby thioammeline is formed in small quantity. This does not interfere with the success of the preparation, as its separation from the chief product is a simple matter.

Pure dicyanodiamide was used in preliminary experiments to determine the best conditions, but from an economic point of view the commercial material may be conveniently employed.

The sample used in the following preparation contained dicyanodiamide = 95.5,\* calcium carbonate = 3.25, melamine = 1.25 per cent.

An intimate mixture of 43.5 grams of dicyanodiamide (=42 grams, pure) and 76 grams of dry ammonium thiocyanate in coarse powder was heated in a tall, narrow beaker partly immersed in a glycerol-bath. A loose cardboard cover carried a thermometer, which served at the same time as a stirrer. At about 80°, the mixture began to melt; the temperature was gradually raised to 120°, about seventy minutes being required for the purpose, and this temperature was maintained for three and a-half hours. As the reaction proceeded, the product, which in the earlier stages was an almost clear liquid, gradually became very viscous. It was now treated, without previous cooling, with about 250 c.c. of water and allowed to digest until cold. After filtration and washing, 7.4 grams of amorphous residue were separated (residue A). The filtrate was concentrated as far as possible by evaporation at 100°, and the crystalline mass which formed on cooling weighed, when dry, 110 grams (Found: SCN=47.76; guanidine thiocyanate requires SCN=49.15 per cent.). The product was redissolved in about 200 c.c. of warm water, and 1.02 grams of amorphous solid (residue B) were separated by filtration.

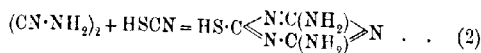
The filtrate was evaporated to a syrupy consistency at 100°, and after "seeding" the cold solution with a minute crystal of guanidine thiocyanate, it quickly set to a crystalline mass of the pure salt (Found: SCN=48.96 per cent.). The yield of pure

\* A single recrystallisation of commercial crude dicyanodiamide is generally sufficient to obtain a product of this degree of purity. The material should be free from calcium hydroxide, which is occasionally present.

guanidine thiocyanate was 107.1 grams, equal to 90.8 per cent. of the theoretical.

The characteristic picrate was prepared as a means of identification. Whilst residue A contained the impurities originally present in the dicyanodiamide, 5.4 grams of pure thioammeline,  $C_3H_5N_3S$ , were separated from it by treatment with sodium hydroxide solution and precipitation, after filtration, by carbon dioxide. It was identified by its properties, as described by Klason (*J. pr. Chem.*, 1886, [ii], **33**, 290). The picrate melted at  $215^\circ$ , and as it separated from solution in peculiar, crystalline formations, which, under the microscope, resembled a highly divided palmatifid leaf, this compound may be used for the identification of the substance.

Since thioammeline results from the interaction of dicyanodiamide and thiocyanic acid, according to the equation



it is not possible to suppress its formation, as dissociation of ammonium thiocyanate to a small extent cannot be avoided under the conditions of the experiment.

Residue B was pure thioammeline, generated as above from small quantities of dicyanodiamide and ammonium thiocyanate which had escaped change. This was proved by evaporating to dryness at  $100^\circ$  a solution of 2 grams of dicyanodiamide and 3.6 grams of ammonium thiocyanate in 50 c.c. of water, when 0.29 gram of thioammeline was obtained. For this reason, evaporation of the solution to dryness in the first instance was found to be the most efficient method for preparing a pure product, and the addition of about a gram of ammonium thiocyanate to the fusion when the reaction has been in progress for two hours is advisable. When an excess of the salt was used at the outset of the experiment, the yield of thioammeline was increased.

Should the crystals of guanidine thiocyanate show opalescence after crystallisation from, and while still in, the mother liquor, a second solution and filtration is necessary to remove the last traces of thioammeline. On account of the great solubility of guanidine thiocyanate in water, its complete separation in crystalline form is tedious; it may be recovered as carbonate by mixing the viscous mother liquor with about four volumes of alcohol, and, after the addition of the requisite amount of potassium hydroxide, the guanidine is precipitated by a current of carbon dioxide.

Apart from its practical value, the reaction is of theoretical interest, since it is obvious that depolymerisation of dicyanodiamide

must be the first phase of the change in order to yield guanidine in such quantity as required by equation (1), whilst the formation of thioammeline, the constitution of which has been clearly demonstrated by Klason (*loc. cit.*), according to equation (2), would be difficult to explain on the basis of the "cyanoguanidine" structure of dicyanodiamide.

Considering that Bamberger and Dieckmann (*loc. cit.*) obtained diguanide by heating guanidine hydrochloride at 185°, there can be no doubt that the latter was first formed in their preparation of diguanide from dicyanodiamide. This has been verified from qualitative experiments, which, however, were of no practical interest; on the other hand, very encouraging results have been obtained in the preparation of methyl- and ethyl-guanidine, an account of which is reserved for a future communication.

So far as the authors are aware, none of the methods hitherto described for the preparation of guanidine can compare with the process now set forth, either in respect of cost, simplicity, or yield of pure product. In this connexion, it may be useful to recount the authors' experience of Ulpiani's method (1909, D.R.P. 209431) for the preparation of guanidine nitrate by the action of aqua regia at 60–65° on dicyanodiamide. A quantitative yield is claimed. Since the change (indirect oxidation) is accompanied by the evolution of much carbon dioxide and nitrogen from dicyanodiamidine simultaneously produced, the maximum yield of guanidine is represented by the ratio  $C_2H_4N_4 \rightarrow CH_5N_3.HNO_3$ ; from three carefully conducted experiments, the best yield was 26 grams of guanidine nitrate from 42 grams of pure dicyanodiamide, equal to 42.7 per cent. of the theoretical calculated on the foregoing ratio. It is evident from this result that not less than two molecules of dicyanodiamide are involved in the production of one of guanidine by this method.

The assay of dicyanodiamide was conveniently conducted by hydrolysis, as follows: 2 grams of the powdered sample were mixed with 25 c.c. of water, *N*-hydrochloric acid was added until the alkaline impurities were neutralised, using methyl-orange as indicator, after which the product was heated for forty-five minutes at 100° with 25 c.c. of *N*-acid. The residual acidity was determined by titration with *N*-sodium hydroxide. Each c.c. of *N*-acid neutralised is equal to 0.084 gram of dicyanodiamide.

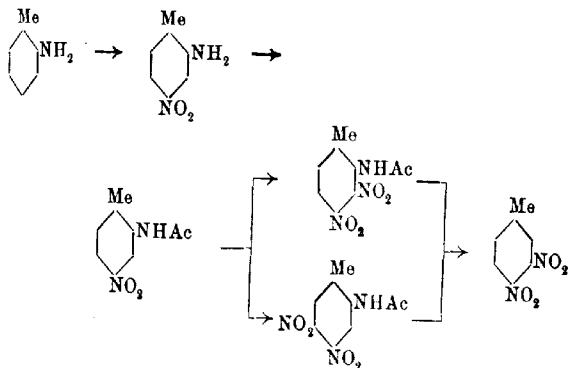
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[Received, August 24th, 1920.]

CXXVIII.—*The Synthesis of some Nitro-derivatives of Toluene.*

By OSCAR LISLE BRADY and PERCY NOEL WILLIAMS.

IN the course of an investigation it was found necessary to prepare a considerable quantity of pure 3:4-dinitrotoluene. This compound is formed with the 2:3- and 2:5-isomerides by the nitration of *m*-nitrotoluene, and can be readily separated from the mixture by freezing (Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 25; Haeussermann and Grell, *Ber.*, 1894, **27**, 2209; Holleman and Sirks, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 280). This method is satisfactory, although the yields are not large. Haeussermann and Grell (*loc. cit.*) mention the preparation from 3-nitro-*p*-toluidine by the Sandmeyer reaction, but do not give details. As a trial of Haeussermann and Grell's method did not give good results, and as *m*-nitrotoluene was unobtainable at the time and its preparation on a laboratory scale was very tedious, other methods of preparation of 3:4-dinitrotoluene were considered. The present paper deals with one of these methods. The starting material was *o*-toluidine, and the reactions involved may be summarised as follows:



The nitration of *o*-toluidine to 4-nitro-*o*-toluidine has been described by Noelting and Collin (*Ber.*, 1884, **17**, 265), but by a modification of their process, the separation of the isomeric nitro-toluidines formed has been greatly simplified. The yields obtained to the stage of the dinitrotoluidines were satisfactory, but the

removal of the amino-group from these compounds did not prove as easy as experience with similar compounds had led the authors to expect, and the yield of 3:4-dinitrotoluene was disappointing. On the other hand, the oxidation of the amino-group in the dinitrotoluidines to the nitro-group by means of Caro's acid proceeds very smoothly and provides a convenient method of synthesis of 2:3:4- and 2:4:5-trinitrotoluenes, which hitherto have been obtained only by the nitration of *m*-nitrotoluene and separation of the two isomerides by fractional crystallisation (Hepp, *Annalen*, 1882, 215, 366) or by nitration of the rare 2:3- and 2:5-dinitrotoluenes (Will, *Ber.*, 1914, 47, 704).

#### EXPERIMENTAL.

**4-Nitroaceto-*o*-toluidide.**—One hundred grams of *o*-toluidine were dissolved in 1087 c.c. of sulphuric acid (D 1·8), care being taken to avoid rise of temperature. The mixture was cooled below 0° in a freezing mixture, and a mixture of 163 c.c. of sulphuric acid (D 1·8) and 50·8 c.c. of nitric acid (D 1·42) cooled to 0° slowly run in so that the temperature did not rise above 0°. When all the acid had been added, the mixture was allowed to remain for one hour. At this stage Noeltzing and Collin (*loc. cit.*) neutralised all the acid with sodium hydroxide. A more economical method which avoids a great increase in the bulk of the liquid and the formation of tarry products consists in adding to the nitration mixture one-half its bulk of water with thorough cooling and stirring. On keeping, the sulphate of 4-nitro-*o*-toluidine separated, and was removed by filtration and washed with alcohol. The yield of sulphate was about 60 per cent. of the theoretical. The 6-nitro-*o*-toluidine formed during the nitration (Green and Lawson, *T.*, 1891, 59, 1011, say 20 per cent.) remained in the filtrate. The sulphate was ground in a mortar with a slight excess of 10 per cent. sodium hydroxide, and the free base collected, washed thoroughly with water, dried, and acetylated with acetic anhydride.

**Nitration of 4-Nitroaceto-*o*-toluidide.**—A solution of 20 grams of 4-nitroaceto-*o*-toluidide in 60 c.c. of concentrated sulphuric acid was added slowly with stirring to 60 c.c. of nitric acid (D 1·5) cooled in ice. When all the solution had been added, the mixture was allowed to remain in ice for thirty minutes, and then poured into 4 litres of ice-water. The solid separating was collected at once and thoroughly washed by grinding three or four times in a mortar with water and filtering. A 70 to 80 per cent. yield of the mixed dinitroaceto-*o*-toluidides was obtained.

**Separation of the Dinitro-*o*-toluidines.**—Fifty grams of the mix-

ture of dinitroaceto-*o*-toluidides were hydrolysed by heating for four or five hours on the water-bath with a mixture of 200 c.c. of concentrated sulphuric acid and 400 c.c. of water. On cooling the mixture, filtering, and washing the precipitate, first with 50 per cent. sulphuric acid and then with water, a 45 per cent. yield of a substance melting at 122° was obtained. On diluting the filtrate, a 25 per cent. yield of a material melting at 150–170° was precipitated. The compound melting at 122° was recrystallised several times from alcohol until the product was of constant melting point, and oriented by conversion into 2:3:4-trinitrotoluene (see below). 3:4-Dinitro-*o*-toluidine crystallises in lustrous, yellowish-brown needles melting at 131–131·5° (Found: N=21·5.  $C_7H_7O_4N_3$  requires N=21·3 per cent.).

The substance melting at 150–170° was recrystallised twice from alcohol and oriented by conversion into 2:4:5-trinitrotoluene (see below). 4:5-Dinitro-*o*-toluidine crystallises in yellow needles melting at 191–191·5° (Found: N=21·6.  $C_7H_7O_4N_3$  requires N=21·3 per cent.).

*Preparation of 3:4-Dinitrotoluene.*—For this purpose it is not necessary to separate the mixture of dinitro-*o*-toluidines, as both give 3:4-dinitrotoluene on removal of the amino-group. Nine grams of the mixture were dried and dissolved in a mixture of 180 c.c. of freshly distilled absolute alcohol and 45 c.c. of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide). The solution was heated on the water-bath, and 27 grams of finely powdered dry sodium nitrite were added in small portions with vigorous shaking. When all the nitrite had been added, the mixture was heated for five minutes, cooled, and diluted with water. The oily solid which separated was crystallised first from hot nitric acid (D 1·4) to destroy tarry matter, and then from alcohol with the addition of animal charcoal, when pure 3:4-dinitrotoluene was obtained. The yield was not good, 2 grams only being obtained from 9 grams of the mixture of dinitrotoluidines.

*Preparation of 2:4:5-Trinitrotoluene.*—To Caro's acid, prepared from 10 grams of ammonium persulphate and 7 c.c. of concentrated sulphuric acid poured on 20 grams of crushed ice, a solution of 2 grams of 4:5-dinitro-*o*-toluidine (m. p. 191°) in 10 c.c. of 80 per cent. sulphuric acid was added. A clear solution was obtained which, on keeping overnight, deposited dinitronitroso-toluene; it was then diluted with water, and the precipitated nitroso-compound added to ten times its weight of nitric acid (D 1·5) and warmed until red fumes were no longer evolved. On cooling and diluting the solution, a crystalline precipitate of 2:4:5-trinitrotoluene was obtained which, after one recrystallisa-

tion from alcohol, was pure. The yield was about 80 per cent. of the theoretical.

*Preparation of 2:3:4-Trinitrotoluene.*—A solution of 3:4-dinitro-*o*-toluidine in 80 per cent. sulphuric acid was added to Caro's acid as above; in this case, however, the amine was precipitated by the dilution of the sulphuric acid, so the mixture was transferred to a stoppered bottle and left for four days, with frequent shaking. At the end of that time the precipitate was collected and treated with nitric acid, as in the previous case, when 2:3:4-trinitrotoluene was obtained in good yield.

The authors wish to express their thanks to the Director of Artillery for permission to publish this work.

RESEARCH DEPARTMENT,  
ROYAL ARSENAL,  
WOOLWICH.

[Received, August 27th, 1920.]

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CXXIX—*Studies in Ring Formation. Part III. The Condensation of Aromatic Amines with  $\alpha$ - and  $\beta$ -Diketones and with 4:4'-Diacetyldiphenyl.*

By CLARENCE VICTOR FERRISS and EUSTACE EBENEZER TURNER.

*The Condensation of Benzidine and Toluidine with Benzil and Glyoxal.*

CONDENSATION products of benzidine and toluidine with benzil or glyoxal were described by Cain and Micklethwait (T., 1914, 105, 1437), but the present authors, after carefully repeating their experiments, are unable to confirm the formulae assigned by them to the products obtained from benzidine and these two diketones.

Whilst the condensation product from benzil and benzidine has now been obtained in a state of purity, its complete analysis and a determination of its molecular weight by the cryoscopic method have not led to any definite conclusions as to its structure. Condensation seems to take place in a more complex manner than is assumed by the above authors. Hydrolysis of the product with mineral acid showed that more molecules of benzil than of benzidine enter into the reaction. Again, although such a condensation might be expected to proceed quantitatively, we have not succeeded in obtaining more than 70 per cent. of the calculated

yield, nor is an appreciable quantity of acetylbenzidine formed, as might be supposed.

Of the products obtained from glyoxal, that formed with benzidine is a highly insoluble non-crystalline mass of unknown molecular complexity. The condensation of glyoxal and tolidine gave a substance of the empirical formula found by Cain and Micklethwait, but its insolubility renders a molecular-weight determination impossible, so that it may possibly be formed by the condensation, not of one molecule of glyoxal with one of tolidine, but by the condensation of two molecules of each together.

*The Condensation of Amines and Diamines with Acetylacetone and Benzoylacetone.*

Condensation products of acetylacetone and benzoylacetone with benzidine and other bases have previously been described by one of us (T., 1915, 107, 1495; 1917, 111, 1). Further examples have now been studied. Among other results, it has been found that *monoacetylisopropylidenetolidine* is a liquid at the ordinary temperature, and *diacetylisopropylidenetolidine* a solid melting at 108° (uncorr.), whereas the corresponding compounds from benzidine melt respectively at 137° and 198° (compare benzylidene-*o*-toluidine, a liquid, and benzylideneaniline, m. p. 48—49°).

Combes (*Bull. Soc. chim.*, 1888, [ii], 49, 89), who first studied the action of amines on acetylacetone, stated that the product of condensation of *p*-toluidine and acetylacetone melted at 39—40°, apparently referring to the trimethylquinoline formed by its further condensation in the presence of sulphuric acid. Pfizinger (*J. pr. Chem.*, 1888, [ii], 38, 40) gives the melting point of the trimethylquinoline in question as 63—64°. The present authors have found that *p*-toluidine and acetylacetone condense under the influence of heat alone to give the trimethylquinoline, the melting point of which is 64°, a fact which renders *p*-toluidine an abnormal compound as regards its action on acetylacetone.

*Ketones of the Diphenyl Series. Attempts to Condense 4:4'-Diacetyldiphenyl with o-Phenylenediamine.*

Hitherto our knowledge of ketones derived from diphenyl has been restricted to phenylacetophenone, 4-phenylbenzophenone, 4:4'-dibenzoyldiphenyl, diphenyl benzyl ketone, and diphenyl  $\alpha$ -naphthyl ketone. Satisfactory proof of the constitution of these ketones has only been given in the case of 4:4'-dibenzoyldiphenyl. This substance, originally obtained by Wolf (*Ber.*, 1881, 14, 2031)



by the action of benzoyl chloride on diphenyl in the presence of aluminium chloride, was prepared by Ullmann (*Annalen*, 1904, **332**, 79) from 4-iodobenzophenone and copper bronze, and thus shown to be the 4:4'-derivative. From this it follows that Wolf's phenylbenzophenone is a 4-derivative.

Various errors have been noticed in the literature, traceable to the work of Adam (*Ann. Chim. Phys.*, 1886, [vi], **15**, 224). This author, as a result of a more or less systematic study of the Friedel and Crafts reaction in the diphenyl series, concluded that in all such reactions, save one, 3-substituted diphenyls were produced, a conclusion based on the fact that these compounds gave, on oxidation, an acid melting at 160–161°, which Adam took to be diphenyl-3-carboxylic acid. His one exception, diphenylbenzophenone, obtained from carbonyl chloride and diphenyl, proved to be identical with the product obtained by Weiler (*Ber.*, 1873, **6**, 1181) from methylal and diphenyl, and gave on oxidation an acid (diphenyl-4-carboxylic) melting at 217–218°.

Adam's phenylacetophenone was stated by Vorländer (*Ber.*, 1907, **40**, 4535) to be the 4-derivative, since derived compounds formed anisotropic liquids, a property which would not be possessed by 3-derivatives.

The action of acetyl chloride on diphenyl in the presence of aluminium chloride has now been shown to result in the formation of 4-phenylacetophenone (m. p. 121°) and 4:4'-diacetyldiphenyl (m. p. 190–191°). The former (identical with Adam's phenylacetophenone) gives, on oxidation, diphenyl-4, and not, as stated by Adam, diphenyl-3-carboxylic acid. The constitution of these ketones has been set beyond doubt by their synthesis, respectively, from 4-cyano- and 4:4'-dicyano-diphenyl by means of magnesium methyl iodide.

Since Adam's phenylacetophenone is the 4-derivative, and since his supposed 3-ethyldiphenyl gave this ketone on partial oxidation, this ethyl derivative must be 4-ethyldiphenyl. It is evident, similarly, that his supposed 3-methyldiphenyl is actually 4-methyldiphenyl.

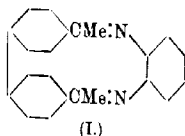
Again, the diphenyl benzyl ketone obtained by Päpcke (*Ber.*, 1888, **21**, 1339) by the action of phenylacetyl chloride on diphenyl in the presence of aluminium chloride, has now been shown definitely to be the 4-derivative by its synthesis from 4-cyano-diphenyl and magnesium benzyl chloride.

In addition, 4:4'-diphenyldiacetyldiphenyl, which is not produced to any extent in the Friedel and Crafts reaction mentioned above, has been prepared from 4:4'-dicyanodiphenyl.

It is evident from the above that in all known Friedel and

Crafts' reactions between diphenyl and halogen compounds, 4-derivatives are obtained, a fact which justifies Schmidlin and Garcia-Banús (*Ber.*, 1912, **45**, 3183) in their assumption as to the constitution of the diphenyl  $\alpha$ -naphthyl ketone prepared by them.

This investigation into the ketones of the diphenyl series was made as the result of desiring to determine the spatial relation of the two acetyl groups in 4:4'-diacetyldiphenyl; this ketone might be expected, if the Kauffer formula for derivatives of diphenyl is valid, to condense with *o*-phenylenediamine to give a compound of the constitution (I). When the two substances in



question are warmed together in acetic acid solution, condensation occurs, and a yellow solid is precipitated from the mixture on adding methyl or ethyl alcohol. As in the case of the condensation product of benzil and benzidine, however, it has not been found possible to ascribe a definite constitution to the product obtained, although the evidence is probably in favour of a compound formed by the condensation of two molecules of ketone with one of diamine.

#### EXPERIMENTAL.

##### *Condensation of Benzil with Benzidine.*

This condensation has been carried out as described by Cain and Micklethwait (*loc. cit.*), 1.84 grams of benzidine, 2.1 grams of benzil, and 10 c.c. of glacial acetic acid being used. After twenty minutes' heating of this mixture on the boiling-water bath, it was cooled and scratched, when the canary-yellow precipitate separated, further warming then causing further separation of precipitate. The yield was found to be increased by periodic cooling and scratching. The precipitate was collected, washed with a little glacial acetic acid and then with dilute acetic acid, and dried in a vacuum over potassium hydroxide. The greenish-yellow solid so obtained (equivalent in quantity to a 70 per cent. conversion to the supposed compound) crystallised readily from benzene, but a less green product was obtained using xylene as solvent, the crystals being then washed with light petroleum [Found: C=85.1; H=5.5. C=85.2; H=5.7. N=5.3, 5.3 per cent. M.W. (by cryoscopic method in bromoform)=496].

The *substance* is readily soluble in hot xylene, benzene, or pyridine, and almost insoluble in cold xylene, benzene, alcohol, or glacial acetic acid.

An attempt to obtain Cain and Micklethwait's ethyl alcohol additive compound was made as follows: the condensation product was collected, dissolved in benzene, the solution evaporated to dryness after the addition of a little alcohol, and the residue again treated with alcohol and the latter evaporated. Evaporation of the benzene solution obtained as above, without adding alcohol, gave a well-defined product identical with that obtained in the presence of alcohol (Found: C=85.0; H=5.5; N=5.7 per cent.).

The *substance* melted at 239–240°, a mixture with the product from xylene (above) melting at the same temperature.

Similarly, an attempt was made to prepare Cain and Micklethwait's methyl alcohol additive compound, following their described method as closely as possible. The product could not be melted under methyl alcohol even on prolonged boiling, and, when dried, melted at 231–234° (Found: C=80.0; H=4.2; N=5.8 per cent.).

The product was again treated with methyl alcohol (for the fourth time), and the whole evaporated (Found: C=80.4; H=3.9 per cent.; m. p. 231–234°).

It was then crystallised from xylene (Found: C=81.3; H=4.9 per cent.; m. p. 233–236°), a second crystallisation from xylene giving a product melting at 234–237° (Found: C=83.7; H=5.0 per cent.).

The present authors attribute the low melting point, etc., of the first of these products to the fact that the green impurities were still present, and the subsequent results to the removal of those impurities.

In order, if possible, to throw more light on the condensation just described, the melting points of mixtures of benzil and benzidine have been determined. The benzil used was purified by recrystallisation from alcohol, and melted at 94.4°. The benzidine was purified by recrystallisation successively from water and dilute alcohol, and then several times from alcohol. Pure benzidine obtained in this way melts at 127.4°. All mixtures of benzil and benzidine melted below the latter temperature, the curve of mixed melting points being part of an inverted parabola, the axis of which ran vertically from the point representing two molecules of benzil to one of benzidine. No evidence for the formation of a compound was forthcoming.

*Condensation of Benzidine with Glyoxal.*

On effecting the condensation as described by Cain and Micklethwait, a dark brown, amorphous precipitate was obtained. On drying, it gave a hard mass, an examination of which gave no results worth recording.

*Condensation of Tolidine with Glyoxal.*

This condensation gave the results published by Cain and Micklethwait (Found: C=82.2; H=5.9; N=12.2. Calc. for  $C_{16}H_{14}N_2$ : C=82.0; H=6.0; N=12.0 per cent.). It was not found possible to carry out a determination of molecular weight, so that the constitution of the substance cannot be deduced.

*Condensation of Acetylacetone with p-Toluidine.*

A mixture of *p*-toluidine and acetylacetone in molecular proportions was gently boiled for an hour. On cooling, the whole set solid, a small portion, after being left in contact with porous porcelain, melting at  $64^\circ$ , and at the same temperature after crystallisation from light petroleum. Almost the theoretically possible yield of 2:4:6-trimethylquinoline was thus obtained (Found: N=8.2. Calc.: N=8.2 per cent.).

*Monoaetylisopropylidenetolidine and its p-Nitrobenzylidene Derivative,  $NO_2 \cdot C_6H_4 \cdot CH:N \cdot C_6H_3Me \cdot C_6H_3Me \cdot N:CMe \cdot CH_2Ac$ .*

A boiling solution of 2.1 grams of tolidine in 15 c.c. of xylene was slowly treated with 1 gram of acetylacetone dissolved in 5 c.c. of xylene, heating being continued for a further hour. On distilling off the xylene, a dark, viscid liquid was obtained, which could not be caused to crystallise. In order to confirm its constitution, it was converted into the *p*-nitrobenzylidene derivative by boiling it in alcoholic solution with a slight excess of *p*-nitrobenzaldehyde. The brick-red precipitate obtained in this way was crystallised from a mixture of pyridine and alcohol (Found: N=10.5.  $C_{26}H_{25}O_3N_3$  requires N=9.8 per cent.).

The high percentage of nitrogen found was due to the presence of a small quantity of di(*p*-nitrobenzylidene)-tolidine, which, when working with barely sufficient material, cannot readily be removed.

*N-p-Nitrobenzylidenemonoaetylisopropylidenetolidine* melts at  $245-247^\circ$ , is readily soluble in hot pyridine, and sparingly so in cold alcohol or acetone.

*Diacetylisopropylidenetolidine, ( $\text{C}_6\text{H}_5\text{Me}\cdot\text{N}:\text{CMe}\cdot\text{CH}_2\text{Ac}$ )<sub>2</sub>.*

A solution of tolidine (8 grams) in 15 grams of acetylacetone was heated at the boiling point for three hours, the excess of diketone distilled off, and the yellow, crystalline residue obtained on cooling crystallised from a mixture of xylene and light petroleum, from which it separated in yellow needles melting at  $108^\circ$  (uncorr.) (Found:  $\text{N}=7.7$ .  $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_2$  requires  $\text{N}=7.4$  per cent.).

*2:4:8:2':4':8'-Hexamethyl-6:6'-diquinolyl.*

The preceding compound was heated with ten times its weight of concentrated sulphuric acid at  $125^\circ$  for two hours, the cooled solution poured into water, the resulting solution rendered alkaline, and the white precipitate collected and crystallised from xylene (Found:  $\text{N}=8.4$ .  $\text{C}_{24}\text{H}_{24}\text{N}_2$  requires  $\text{N}=8.2$  per cent.).

The base crystallises from xylene in minute cubes melting at  $252.5^\circ$ , and is almost insoluble in either hot or cold alcohol, carbon tetrachloride, or toluene.

The *platinichloride* was obtained in the usual manner, and forms brownish-yellow needles (Found:  $\text{Pt}=26.2$ .  $\text{C}_{24}\text{H}_{24}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=26.14$  per cent.).

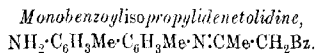
*Monobenzoylisopropylidenbenzidine,*  
 $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CMe}\cdot\text{CH}_2\text{Bz}.$ 

A solution of 3.24 grams of benzoylacetone in 15 c.c. of xylene was added gradually to a boiling solution of 3.68 grams of benzidine in 15 c.c. of xylene, the heating continued for a further hour, the solvent removed by distillation, and the yellow residue crystallised from a mixture of pyridine and alcohol, when it separated in slender, pale yellow needles melting at  $179^\circ$  (Found:  $\text{N}=8.7$ .  $\text{C}_{22}\text{H}_{20}\text{ON}_2$  requires  $\text{N}=8.5$  per cent.).

*Acetylisopropylidenbenzoylisopropylidenbenzidine,*  
 $\text{CH}_3\text{Ac}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CMe}\cdot\text{CH}_2\text{Bz}.$ 

A boiling solution of the preceding compound (0.761 gram) in 10 c.c. of xylene was slowly treated with a solution of 0.232 gram of acetylacetone in 5 c.c. of xylene, and the reaction allowed to complete itself during a further short boiling. On removing the xylene by distillation, a yellow residue remained, which was crystallised from a mixture of pyridine and alcohol (Found:  $\text{N}=7.0$ .  $\text{C}_{27}\text{H}_{26}\text{O}_2\text{N}_2$  requires  $\text{N}=6.8$  per cent.).

The compound forms yellow leaflets melting at 234–236°, and sparingly soluble in alcohol, readily so in cold chloroform, and dissolves in hot pyridine.



This substance was obtained in a manner similar to that described for the corresponding benzidine compound, and crystallises from a mixture of pyridine and alcohol in pale yellow needles melting at 170°. It acquires a green colour in moist air, owing to partial oxidation (Found: N=8.0.  $\text{C}_{24}\text{H}_{24}\text{ON}_2$  requires N=7.9 per cent.).

*Condensation of Acetyl Chloride with Diphenyl.*

(a) *Preparation of 4-Phenylacetophenone.*—Acetyl chloride (8 grams) was mixed with 100 c.c. of carbon disulphide and a large excess of diphenyl (35 grams), and 20 grams of anhydrous aluminium chloride were slowly added. The reaction was carried to completion by heating, and the cooled mixture decomposed with ice and dilute hydrochloric acid. The carbon disulphide was removed in a current of steam, and the residue cooled, filtered, and dried. The white solid so obtained was extracted with boiling light petroleum until a sample of the residue, on drying, melted at 115–120°. The residue, consisting of almost pure phenylacetophenone, was crystallised from alcohol, and melted at 120–121° (uncorr.). It possessed the properties ascribed to it by Adam (*loc. cit.*) (Found: C=85.2; H=6.2. Calc.: C=85.7; H=6.1 per cent.).

(b) *Preparation of Phenylacetophenone and 4:4'-Diacetyl-diphenyl.*—Anhydrous aluminium chloride (26.7 grams) was covered with a mixture of 100 c.c. of carbon disulphide and 15.4 grams of diphenyl. Acetyl chloride (15.7 grams) was then slowly added, and the evolution of hydrogen chloride allowed to become complete by subsequent heating in warm water. The carbon disulphide was evaporated, the mixture decomposed as before, and the resulting white solid collected and dried. Elaborate fractional crystallisation from alcohol gave phenylacetophenone (moderately soluble) and 4:4'-diacetyldiphenyl (sparingly soluble). The latter was purified by crystallisation successively from dilute acetic acid, alcohol, and carbon tetrachloride; it forms almost colourless leaflets melting at 190–191° (uncorr.) (Found: C=80.5; H=5.9.  $\text{C}_{16}\text{H}_{14}\text{O}_2$  requires C=80.7; H=5.9 per cent.).

*Preparation of 4-Cyanodiphenyl.*

The preparation of this substance from diazotised 4-amino diphenyl and potassium cuprocyanide proved unsatisfactory, a large quantity of a polymeride being formed. It is interesting to note that Kaiser (*Annalen*, 1890, **257**, 100) obtained a moderately good yield of diphenyl-5-carboxylic acid by the hydrolysis of the total crude product. The method described by Rassow (*Annalen*, 1894, **282**, 143) for the preparation of the nitrile was finally adopted; it is, however, tedious, and gives a large quantity of the polymeride.

*Preparation of 4-Phenylacetophenone (4-Acetyldiphenyl).*

A solution of 0.3 gram of 4-cyanodiphenyl in 100 c.c. of benzene was added to a Grignard reagent prepared from 1.5 gram of methyl iodide, 0.24 gram of magnesium, and 40 c.c. of ether. The ether was then removed by distillation, and the residue heated to boiling for four hours, then cooled, decomposed with water and acid, and the benzene layer separated, dried, and evaporated. The residue was extracted with boiling alcohol in the presence of wood charcoal, the extracts filtered, evaporated, and the residue treated as before. In this way, a small quantity of a white solid was obtained, crystallising from alcohol in colourless needles melting at 120—121°, and producing no depression of the melting point of the phenylacetophenone prepared as described above. The latter is therefore 4-phenylacetophenone.

Oxidation under the exact conditions described by Adam (*loc. cit.*) gave a mixture of unchanged ketone and diphenyl-4-carboxylic acid melting at 220°. The latter was extracted from the mixture by means of sodium hydroxide, and the extract filtered and acidified, etc. The low melting point (160—161°) found by Adam was evidently due to the presence of unchanged ketone.

*Preparation of 4-Diphenyl Benzyl Ketone.*

(a) This substance was obtained by condensing diphenyl (1 mol.) with phenylacetyl chloride (2 mols.) in carbon disulphide solution by means of aluminium chloride, the reaction mixture being treated in the usual manner. The black, tarry solid obtained in this way was extracted repeatedly with boiling alcohol, the extracts precipitated with water, and the resulting yellow solid freed from phenylacetic acid by extraction with hot aqueous ammonia. The product was finally crystallised repeatedly from

alcohol, and then melted at 150°. Its properties agreed with those described by Pöpcke (*loc. cit.*).

(b) A solution of 0.9 gram of 4-cyanodiphenyl in 100 c.c. of benzene was added to a Grignard reagent prepared from 2 grams of benzyl chloride, 0.36 gram of magnesium, and 50 c.c. of ether. The latter solvent was removed by distillation, the residue heated to boiling for six hours, and then decomposed in the usual manner. Extraction of the solid finally obtained with light petroleum and benzene gave a white solid melting, after crystallisation from alcohol, at 150°, and producing no depression of the melting point of the product from (a). The latter is therefore 4-diphenylbenzyl ketone.

#### *Preparation of 4:4'-Dicyanodiphenyl.*

This substance has hitherto only been prepared from the corresponding disulphonic acid by fusion with potassium cyanide. The following method was found to be more convenient.

A solution of 17.2 grams of benzidine in 42.5 c.c. of concentrated hydrochloric acid and 150 c.c. of water was diazotised with a concentrated solution of sodium nitrite, and the solution added gradually to a warm solution prepared by mixing 50 grams of cupric sulphate pentahydrate (in 200 c.c. of water) with 55 grams of potassium cyanide (in 100 c.c. of water), benzene being added to prevent the accumulation of froth. The reaction was completed by heating to a hot water-bath temperature, the brown precipitate collected, washed with boiling water, and dried, and then extracted repeatedly with much boiling alcohol; the filtered extracts were reprecipitated with water, and the combined precipitates dried and recrystallised from pyridine. The pure nitrile obtained in this way melts at 235° (uncorr.), as stated by Doebner (*Ber.*, 1876, 9, 272).

#### *4:4'-Diacetyldiphenyl.*

A solution of 2 grams of 4:4'-dicyanodiphenyl in 150 c.c. of benzene was added to a Grignard reagent prepared from 6 grams of methyl iodide, 1 gram of magnesium, and 50 c.c. of ether. The ether was removed by distillation and the residue heated to boiling for six hours, then treated with water and excess of dilute sulphuric acid, and the mixture again heated for an hour, it being thought possible that, owing to the extreme difficulty of hydrolysing the dinitrile (see Doebner, *Annalen*, 1874, 172, 116), the intermediate magnesium additive compound formed in the present reaction would only slowly be decomposed by cold acid (see Forster



and Judd, T., 1905, **87**, 368). The benzene layer was finally separated and dried. When evaporated slightly, it deposited the diacetyldiphenyl in clusters of needles or leaflets melting at  $190^{\circ}$ , and producing no depression of the melting point of the diacetyldiphenyl prepared from diphenyl and acetyl chloride (above). The latter is therefore the 4:4'-derivative.

*4:4'-Diphenyldiacetyldiphenyl.*

A solution of 2 grams of 4:4'-dicyanodiphenyl in 200 c.c. of benzene was added to a Grignard reagent prepared from 7 grams of benzyl chloride, 1 gram of magnesium, and 60 c.c. of ether, when a reddish-brown precipitate was formed. The ether was removed by distillation, the residue heated to boiling for four hours, decomposed with water and dilute acid, again heated, and finally filtered, and the two layers were separated. The residue from the filtration was combined with the residue obtained by evaporating the benzene solution, dried, and crystallised from pyridine, when it formed white leaflets melting at  $224^{\circ}$  (uncorr.) (Found: C=86.7; H=5.6.  $C_{22}H_{12}O_2$  requires C=86.2; H=5.6 per cent.).

Both of the ketones just described react normally with phenylhydrazine.

*Condensation of 4:4'-Diacetyldiphenyl with o-Phenylenediamine.*

When the ketone and the diamine are gently heated together for a few minutes, a red colour is developed, owing to the formation of a *substance*, which is precipitated by alcohol and is insoluble in the latter. Condensation in slightly diluted glacial acetic acid (to preclude the formation, so far as possible, of benziminazole) gave, when equimolecular quantities of the reacting substances were taken, an orange-yellow product, obtained by precipitation of the acetic acid solution with methyl alcohol. On dissolving it in pyridine and precipitating with light petroleum, it was obtained in a microcrystalline condition (m. p. [indefinite] about  $150^{\circ}$ ) (Found: C=84.7; H=5.7; N=4.2.  $C_{18}H_{10}O_2N_2$  [2 mols. of ketone condensing with 1 mol. of base, with elimination of 2 mols. of water] requires C=83.2; H=5.8; N=5.1;  $C_{22}H_{12}N_2$  [1 mol. of ketone, 1 mol. of base, elimination of 2 mols. of water] requires C=85.2; H=5.8; N=9.0 per cent.).

The small quantity of the product rendered a thorough investigation impossible, but it is thought that the evidence indicates the formation of a compound of the iminazole type by the condensa-

tion of two molecules of the diketone with one of *o*-phenylenediamine.

We desire to thank Mr. R. G. Hook for some help with one of the experiments, and the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

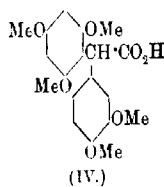
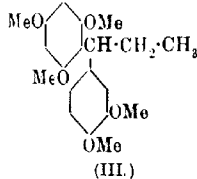
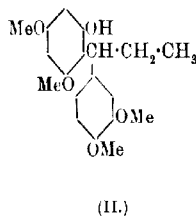
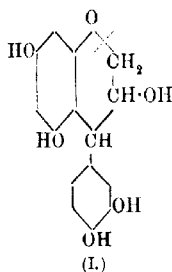
THE UNIVERSITY CHEMICAL LABORATORIES,  
SYDNEY, N.S.W.

[Received, August 30th, 1920.]

### CXXX.—*The Constitution of Catechin. Part II.*

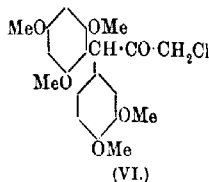
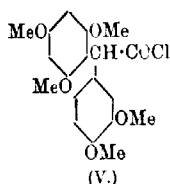
By MAXIMILIAN NIERENSTEIN.

IN the previous communication (this vol., p. 971), provisional formulæ were suggested for catechin (I) and for the methylated reduction product (III) obtained by Kostanecki and Lampe (*Ber.*, 1907, **40**, 720) from catechin tetramethyl ether. At the same time, it was shown that Kostanecki and Lampe's substance may be oxidised to 3:4:2':4':6'-pentamethoxydiphenylacetic acid (IV).

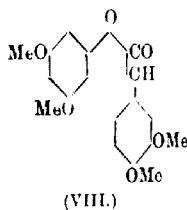
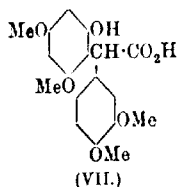


The present communication describes the synthesis of 3:4:2':4':6'-pentamethoxy-*αα*-diphenylpropane (III), which was

found to be identical in every respect with the methylated reduction product of Kostanecki and Lampe. The synthesis was carried out according to the following scheme: 3:4:2':4':6'-pentamethoxydiphenylacetyl chloride (V), on treatment with diazomethane (compare Clibbens and Nierenstein, T., 1915, **107**, 1491), yielded 3:4:2':4':6'-pentamethoxydiphenylmethyl chloromethyl ketone (VI), which, on reduction with metallic sodium and alcohol, gave 3:4:2':4':6'-pentamethoxy- $\alpha\alpha$ -diphenylpropane (III).



The intermediate 2'-hydroxy-3:4:4':6'-tetramethoxy- $\alpha\alpha$ -diphenylpropane (II) has previously not been investigated; thus, Kostanecki and Lampe (*loc. cit.*) only refer to it as an oil, without further mention. It has now been obtained as a crystalline substance, which yields on oxidation 2'-hydroxy-3:4:4':6'-tetramethoxydiphenylacetic acid (VII). The latter substance behaves normally towards methyl sulphate, diazomethane, and acetyl chloride and pyridine, yielding the corresponding derivatives. On digestion with acetic anhydride and anhydrous sodium acetate, however, 3:5:3':4'-tetramethoxy-2-phenylcoumaran-1-one\* (VIII) is formed, which is also produced when 3:4:2':4':6'-pentamethoxydiphenylacetic acid (IV) is treated with acetyl chloride according to Stoermer and Friderici's method (*Ber.*, 1908, **41**, 340).



\* The numbering of the coumaran nucleus is as suggested by Stoermer (*Annalen*, 1900, **312**, 258).

## EXPERIMENTAL.

## 3:4:2':4':6'-Pentamethoxydiphenylacetyl Chloride (V).

Six and a-half grams of 3:4:2':4':6'-pentamethoxydiphenylacetic acid are heated on a water-bath for three hours with 10 grams of thionyl chloride. As much as possible of the unchanged thionyl chloride is distilled off under diminished pressure and the residue dissolved in dry benzene. The solid obtained by evaporating the benzene is left over solid potassium hydroxide in a vacuum for some time, so as to remove the adhering traces of thionyl chloride. The product crystallises from benzene in small clusters of prismatic needles, which melt at 76.5°. The yield is 98 per cent. of the theoretical (Found: Cl=9.6.  $C_{19}H_{21}O_6Cl$  requires Cl=9.3 per cent.).

## 3:4:2':4':6'-Pentamethoxydiphenylmethyl Chloromethyl Ketone (VI).

To a solution of 6 grams of the acyl chloride in dry ether (according to Grignard), an ethereal solution of freshly prepared diazomethane from 30 c.c. of nitrosomethylurethane is added. When the evolution of nitrogen ceases, the same amount of diazomethane is again added, and the solution allowed to remain for several days, moisture being excluded. The ether, which contains an excess of diazomethane, is distilled off, and the residue crystallised from benzene. Large, glistening plates separate, which melt at 102° and have the characteristic odour of the chloromethyl ketones. The yield is 94 per cent. of the theoretical (Found\*: C=60.6; H=5.9; Cl=8.9.  $C_{20}H_{23}O_6Cl$  requires C=60.9; H=5.8; Cl=9.0 per cent.).

3:4:2':4':6'-Pentamethoxy-*aa*-diphenylpropane (III).

A solution of 6 grams of the ketone in about 200 c.c. alcohol is heated on a water-bath with 20 grams of metallic sodium until the latter disappears. The solution is subsequently reduced to about 50 c.c. and diluted with water. The precipitate crystallises from alcohol in small needles, which melt at 83–84°. This melting point is not depressed when mixed with the methylated reduction product of Kostanecki and Lampe (Found\*: C=69.2; H=7.7. Calc.: C=69.3; H=7.5 per cent.).

\* Dried over paraffin in a vacuum.

*2'-Hydroxy-3:4:4':6'-tetramethoxy- $\alpha$ -diphenylpropane* (II).

By distilling Kostanecki and Lampe's reduction product (deoxyhydrocatechin tetramethyl ether) under diminished pressure, the greater proportion is obtained as an oil boiling at 235—238°/10—11 mm. After remaining on ice for a short time, it readily solidifies. A few crystals of this substance are sufficient to cause the oil of other preparations to become semi-solid without previous distillation. Prepared by this method, any adhering oil may be removed by washing with light petroleum and subsequent drying on a porous plate. Three preparations from 10 grams of catechin tetramethyl ether gave 7.8, 6.2, and 8.1 grams, respectively, of the solid.\* It crystallises from alcohol in rectangular plates, which feel oily and melt at 106°. The substance is soluble in the usual organic solvents, with the exception of light petroleum in the cold. The alcoholic solution turns violet with ferric chloride (Found: C=68.5; H=7.4.  $C_{19}H_{24}O_5$  requires C=68.7; H=7.2 per cent.).

On treatment with methyl sulphate, the theoretical yield of 3:4:2':4':6'-pentamethoxy- $\alpha$ -diphenylpropane (III) is obtained. It melts at 83—84°, and this melting point is not depressed when mixed with the methylated reduction product of Kostanecki and Lampe.

*2'-Hydroxy-3:4:4':6'-tetramethoxydiphenylacetic Acid* (VII).

Nine grams of 2'-hydroxy-3:4:4':6'-tetramethoxy- $\alpha$ -diphenylpropane suspended in 300 c.c. of a 20 per cent. solution of potassium hydroxide in water are oxidised on a boiling-water bath for four hours with 9 grams of potassium permanganate dissolved in 200 c.c. of water. The solution is filtered while hot, and, after cooling, acidified with dilute sulphuric acid. The dark-coloured precipitate is not filtered, but the solution extracted several times with ether, in which the precipitate dissolves. The ethereal extract, dried over anhydrous sodium sulphate, leaves a solid on evaporation, which, after several crystallisations from water,

\* The reduction of catechin tetramethyl ether according to the method of Kostanecki and Lampe (*loc. cit.*) is apparently accompanied by some decomposition, since the crude reduction product has an odour of acetic acid. Several attempts were made to isolate some of the disintegration products by extracting the porous plate with alcohol. A small crop of needles was obtained from the alcoholic extract. They melted at 178—180°, which is the melting point given for veratric acid, but there was not enough material to establish their identity.

† Dried over paraffin in a vacuum

animal charcoal being used, yields long, prismatic needles melting at 168—169°, carbon dioxide being evolved. By prolonged drying over phosphoric oxide in a vacuum, or heating at 110°, one molecule of water is lost (Found\*:  $H_2O=5.0$ . Calc.:  $H_2O=4.9$  per cent.). The anhydrous product is powdery in appearance and melts at 172—173°, carbon dioxide being evolved. The substance is also soluble in alcohol or ethyl acetate, but insoluble in benzene or toluene. Both the aqueous and alcoholic solutions turn bluish-violet with ferric chloride. The yield is 78 per cent. of the theoretical (Found\*:  $C=62.2$ ;  $H=5.9$ .  $C_{18}H_{20}O_7$  requires  $C=62.1$ ;  $H=5.7$  per cent.).

On methylation with methyl sulphate, 3:4:2':4':6'-penta-methoxydiphenylacetic acid (IV), melting at 150—151°, is formed. Diazomethane converts 2'-hydroxy-3:4:4':6'-tetramethoxydiphenylacetic acid quantitatively into the corresponding methyl ester, which melts at 119°. Neither of these melting points is depressed when the compounds are mixed with the corresponding substances previously described (*loc. cit.*, p. 879).

The *acetyl* derivative is prepared by the action of acetyl chloride (3 grams) and pyridine (30 grams) on the anhydrous acid (3 grams). It crystallises from alcohol in prismatic needles, which melt at 183—184°, carbon dioxide being evolved (Found\*:  $C=61.5$ ;  $H=5.7$ .  $C_{20}H_{22}O_8$  requires  $C=61.5$ ;  $H=5.6$  per cent.).

### 3:5:3':4'-Tetramethoxy-2-phenylene-m-uran-1-one (VIII).

One gram of 2'-hydroxy-3:4:4':6'-tetramethoxydiphenylacetic acid is digested with 30 c.c. of acetic anhydride and 3 grams of anhydrous sodium acetate, and the mixture subsequently diluted with water. The precipitate obtained in this way crystallises from absolute alcohol in stout, prismatic needles, which melt at 117°. The yield is 85 per cent. of the theoretical (Found†:  $C=65.4$ ;  $H=5.5$ .  $C_{18}H_{18}O_6$  requires  $C=65.5$ ;  $H=5.4$  per cent.). The same product is also obtained when 3 grams of 3:4:2':4':6'-penta-methoxydiphenylacetic acid, dissolved in 20 c.c. of glacial acetic acid, are kept at the ordinary temperature for forty-eight hours with 50.4 c.c. of a solution of 100 c.c. glacial acetic acid and 2.12 grams of acetyl chloride (1 mol. of acetyl chloride). The greater part of the acetic acid is removed under diminished pressure and the residue precipitated with water. The product crystallises from absolute alcohol in stout, prismatic needles, which melt at 117°.

\* Dried at 110°.

† Dried over paraffin in a vacuum.

and this melting point is not altered on mixing with the previous preparation. The yield is 91 per cent. of the theoretical.

The author is indebted to the Colston Society of the University of Bristol for a grant which has covered the expenses of this research.

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[Received, September 9th, 1920.]

*Note added October 1st, 1920.*—Since this communication was submitted, a paper by Freudenberg (*Ber.*, 1920, **53**, [B], 1416) has appeared, in which he describes 3:4:2':4':6'-pentamethoxy- $\alpha\gamma$ -diphenylpropane as melting at 87–88°, which is the melting point given by the author (this vol., p. 972) for this substance. Freudenberg states, further, that Kostanecki and Lampe's methylated reduction product also melts at 87–88°, which is not correct. This substance melts at 83–84°, as given by Kostanecki and Lampe (*Ber.*, 1902, **40**, 720). The author has on five separate occasions prepared this product, and has always found it to melt at 83–84°. No difference of the melting point has been recorded by Ryan and Walsh (*Sci. Proc. Roy. Dublin Soc.*, 1916, **15**, 120) who have also prepared Kostanecki and Lampe's product. In view of Freudenberg's assumption that Kostanecki and Lampe's methylated reduction product is identical with 3:4:2':4':6'-pentamethoxy- $\alpha\gamma$ -diphenylpropane, the following mixed melting points were taken. They clearly disprove his contentions. (1) Kostanecki and Lampe's methylated reduction product (m. p. 83–84°) and 3:4:2':4':6'-pentamethoxy- $\alpha\gamma$ -diphenylpropane (m. p. 87–88°) giving a depression of 9 to 11 degrees. Similar results were obtained (August 11th, 1919) when three mixed melting points of these two substances were taken. (2) On the other hand, a mixture of Kostanecki and Lampe's product (m. p. 83–84°) with 3:4:2':4':6'-pentamethoxy- $\alpha\alpha$ -diphenylpropane (m. p. 83–84°), described in the present communication, melted at 83–84° without the slightest depression, as already observed (April 26th, 1920), when two mixed melting points of these substances were taken.







[To face p. 1157 Text]

## EMIL FISCHER MEMORIAL LECTURE.

DELIVERED ON OCTOBER 28TH, 1920.

By MARTIN ONSLOW FORSTER, F.R.S., Treasurer.

To a world confused and lacerated by the bitter consequences of protracted warfare, at a time when every element of constructive and harmonising influence was most sorely needed, there came without premonition the announcement that Emil Fischer was dead. Inured as the nations had become to loss and disaster, it was probably with surprise that the scientific communities found the misfortune with which they were now confronted to be one in common with their former enemies. For the place which he occupied in our minds, first attained by his mastery of our subject, was hallowed by regard for his sterling disposition, compassion for his griefs, admiration for his outstanding power.

Emil Fischer was born on October 9th, 1852, at Euskirchen, some twenty-five miles from Cologne on the south-westerly high-road to the Eifel, about twenty miles from Bonn. Preceded by five sisters, he was the only son of Laurenz Fischer and Julie Poensgen. After leaving school at Bonn in 1869, he was apprenticed to his brother-in-law, Ernst Friedrichs, a timber merchant, but the occupation proving uncongenial, he became a pupil of Kekulé in 1871, and proceeded in the following year from Bonn to Strasbourg. Here he graduated in 1874 under von Baeyer, with whom he passed to Munich in 1875 as an assistant, becoming *Privatdozent*, and soon afterwards succeeding Volhard as *Ausserordentlicher Professor* in 1879. On the transference of Volhard to Halle, he was called to the chair of chemistry at Erlangen in 1882, whence he proceeded in 1885 to Würzburg in succession to the elder Wislicenus. He remained seven years at the Bavarian university, and on the demise of von Hofmann, in 1892, was appointed professor and director of the chemical institute in Berlin University, a post which he filled with increasing distinction until his death, which took place in the night of July 14th, 1919, at Wannsee, his country home. Such, in the barest outline, was Fischer's career—simple, straightforward, and honourable, like his nature.

Amongst those who came in contact with him, the impression left by Fischer is indelible, but the words to describe his personality

do not readily come. Physically commanding, his authority rested on the solid foundation of natural dignity unmarred by self-assertion. The brisk, upright carriage marked the man of action; the glowing eyes revealed his attitude of constant, keen inquiry; the impatience with trivialities was one aspect of his dominating, steadfast control of essentials. With ordinary human perception, it was impossible for anyone to escape his contagious enthusiasm, and yet all the time the master did not obscure the man; for although his daily demeanour was tinged with severity, his heart when revealed was deeply kind, and, in circumstances of relaxation, joyous. The alert presence, the ardent gaze, and the resonant voice will not fade from the recollection of those to whom they became the symbols of a treasured experience.

The salient quality of his life was unswerving singleness of purpose. Rapid satisfaction of reasonable professional ambition and the fact that he was only forty when summoned to Berlin did not distract him from his chosen path. The legitimate pride occasioned by the summons, the glad recognition of increased opportunities for research, the happy anticipation of entering an unlimited scientific environment were tempered by anxiety lest the social and ceremonial demands of the capital city should make serious inroads into the real work of his life. Even his sixtieth birthday celebration was, by his express desire, an almost domestic affair. Had he sought their presence, representatives of foreign academies, captains of industry, and councillors of State would gladly have joined his less exalted admirers in their tribute to the master, but the master himself ordained otherwise; with one exception, all the participants were former students, old colleagues, or members of his household.

Although the strictness with which Fischer confined his energy to affairs of chemistry was temperamental and due primarily to his natural and cultivated taste for the science, it is probable that his condition of health was a contributory factor. In the summer of 1881 he suffered an attack of mercury poisoning, consequent on studying the action between mercuric oxide and aliphatic hydrazines; neither he nor Böslér noticed until too late that mercury diethyl is produced, although the odour did not escape von Baeyer. The direct effects of this incident lasted three months, and ten years later Fischer fell a victim to the insidious onslaught of phenylhydrazine vapour. In his own words: "Dieses allerliebste Bäschen war meine erste und dauerndste chemische Liebe. Wir haben uns 15 Jahre lang ausgezeichnet miteinander getragen, während viele andere Menschen gleich dadurch zu Schade kamen. Aber dann brach auch bei mir das Unglück ein mit einer

chronischen und äusserst hartnäckigen Vergiftung, und es hat 12 Jahre gedauert, bis die Folgen beiseitigt waren."

It is characteristic of the man that his work is devoid of "popular" features, although common experience at every turn traverses the materials with which he dealt. The task of explaining the achievements of other great chemists, Pasteur, von Hofmann, or Sir William Perkin, for example, is relatively simple, but the fellow-citizen cannot hope to understand Fischer's chemistry of the breakfast-table until he has learned that the operations of digestion are essentially chemical transactions of a subtle nature. To the man whose sugar "melts" in tea, and who believes in a second member of the class, beet-sugar, and probably a third, namely, saccharin, how are the beauties of the sixteen stereoisomeric aldohexoses to be revealed? How is it possible to explain to a woman unversed in chemistry the family connexion between her silk dress and a scrambled egg?

In literary style his papers are uncompromisingly ascetic. The reader is quickly made aware of the subject about to be developed; in simple phrases the theme is pursued with a marked absence of verbal ornament, and the treatment, although complete, is so concise that a concluding summary of results is unnecessary. By this restraint Fischer has earned the gratitude of all chemists, for the labour of assimilating his enormous output has been reduced thereby to a minimum. Failing thorough discipline in writing abstracts of scientific memoirs, a study of the literary method adopted by Fischer offers the best possible training for the research chemist, old or young, in preparing reports of his own investigations.

By the time he had passed from Erlangen to Würzburg, Fischer's reputation had become magnetic, and from that period an increasing number of *doctorandi* sought admission to his laboratory. The aggregate of these must be several hundreds, including many nationalities, and with the passage of years he received, in addition to the customary distinctions accorded by his countrymen, the honours which it is the practice of foreign academies to offer. He became an Honorary and Foreign Member of the Chemical Society in 1892, a Foreign Member of the Royal Society in 1899, and an Honorary Member of the Royal Institution in 1904; he received the Davy Medal in 1890, the Nobel Prize for chemistry in 1902, and the Elliott Cresson Gold Medal from the Franklin Institute of Philadelphia in 1913.

Although too rarely seen in this country, he was warmly welcome when he came, and there is every ground for believing that the cordial feeling towards him which certainly existed

amongst British chemists was reciprocated, a concrete illustration of this being given by the fact that his eldest son, Hermann Fischer, passed two terms at Cambridge. Moreover, the many Englishmen who worked in his laboratory were quickly made aware of the kindly feeling towards them which he cherished, an experience adding appreciably to the benefit they derived from the association. Thus the veneration surrounding his name in this country could scarcely have been less, in depth and sincerity, than that acknowledged by his fellow-countrymen. It therefore gave lustre to the Perkin Jubilee in 1906 when, as President of the German Chemical Society, he conveyed the congratulations of that body to the veteran whilst conferring on him the Hofmann Medal.

The following year, in which he delivered the Faraday Lecture, marked another memorable occasion, postponed from 1895, when his condition of health did not permit acceptance of the invitation then given. The title of this address, namely, "Synthetical Chemistry in Relation to Biology," crystallises in a single phrase the profound significance of his own work; for, when reviewed as a chapter which is closed, this must be regarded as having established on a firm basis the fundamental, but bewildering, science of biochemistry. The assimilation of carbon dioxide and water by plants, the variety and complexity of saccharide molecules proceeding therefrom, the degradation of the proteins, the probable course of their synthesis from amino-acids, and the power of assemblage or of disruption exerted by enzymes on all these building materials of the animal and vegetable kingdoms, are subjects which Fischer not merely illuminated, but which he was the first to place in coherent arrangement and intelligible sequence. Recognition of the fact that all this was accomplished, not by revolutionary processes or tortuous theories, but by dexterous development of the thoughts and operations expanded by Liebig, von Hofmann, Pasteur, and von Baeyer, is perhaps the highest tribute which can be paid to his genius. Indeed, it offers the greatest inspiration to less gifted workers, who may thus be encouraged to perceive opportunities for discovery in adroit applications of classical principles: and pursuing methods of such simplicity may even arrive, by those devious paths which unfold themselves with delight and refreshment to an earnest inquirer, unexpectedly, as on the lifting of a curtain, directly at the threshold of a fundamental truth.

The natural curiosity which seeks to account for the biochemical trend of Emil Fischer's researches can only take refuge in predilection. There is nothing to explain it discoverable in family associations or in the tasks of his young manhood. Laurent

Fischer, who passed the age of ninety-four, was an active and enterprising general merchant engaged in supplying the requirements of the peasant farmers inhabiting the Eifel; associated with his brothers, he was also concerned in a spinning mill and a brick-works close to his native town, and in the foundation of a brewery at Dortmund. Thus there existed every inducement for his only son to pursue a business career, and Ernst Friedrichs was quite positive in declaring his conviction that no good would come of Emil when the young apprentice relinquished an opportunity which appeared to him so full of promise. During this abortive attempt to transform him into a timber merchant, Fischer had been occupied with experiments in a home-made laboratory, and contemplated devoting himself to a study of physics; but his father, attracted by the handsome returns which the Rhenish chemical factories were already beginning to show, finally persuaded him to become a chemist.

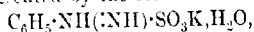
His prepossession in favour of biochemistry was destined to resist another contrary influence. The doctorate thesis dealt with fluorescein and the phthalein of orcin, whilst his work on rosaniline in the Munich days would almost certainly have confirmed a less resolute mind in the pursuit of colour chemistry, then in the early flush of active growth. Moreover, this direction would have been a natural sequence to the powerful influence of von Baeyer, at that time immersed in the problems of indigotin synthesis. Indeed, it is a noticeable feature in the development of his character that Fischer's work detached itself so completely from household authority and so rapidly from early chemical environment. The only conspicuous mark of the training which he owed to von Baeyer was manipulative skill of the very highest order; this was revealed by results achieved with uninviting materials, frequently used in very small quantities, by the inception and adaptation of ingenious experimental devices, and by the rarity of occasion to revise earlier conclusions of his own. Fortunate he undeniably was, but the good fortune was thoroughly well earned by ceaseless industry. He was fortunate, for example, in the fact that nothing resembling the Walden inversion, that *bête noire* of optical activity, disturbed the aldohexose configuration. Imagine the confusion which would have arisen if gluconic and mannonic acids, instead of being smoothly interconvertible when heated with quinoline, had given mixtures of idonic, gulonic, galactonic, talonic, altronic, and allonic acids. Phenylhydrazine was a tremendous *coup*; but the preparation was according to plan, although its remarkable properties were fortuitous, a happy illustration of "to him that hath shall be given."

Nevertheless, that mysterious counterpoise of destiny, from which the greatest and the humblest cannot escape, plunged him into profound sorrow at the meridian of his career. In 1888 he had married Agnes Gerlach, but the happy union was cut short by her death in 1895. Thereafter his three boys were tended by Frln. Margarete Barth, who administered his household for the remaining twenty-four years of his life with watchful solicitude.

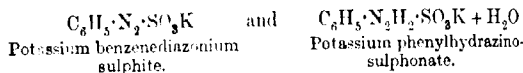
### *Early Work.*

Fischer entered the field of organic chemical research at the opening of its brightest epoch. Largely in consequence of Kekulé's theory of benzene structure, the ground was ready for systematic cultivation: the advent of peace encouraged a willing and increasing band of workers to prepare themselves for fruitful labour; together they stood at the threshold of the imposing structure which was destined to arise during the next forty years.

The act of reading, in 1920, the paper on phenylhydrazine communicated from the Strassbourg laboratory in 1875, engenders the sensation of contemplating the modest source of a mighty river. In 1871, Strecker (with Römer) had treated benzenediazonium nitrate with excess of hydrogen potassium sulphite, obtaining a salt, which he represented by the formula



and giving to diazotised aniline the expression since associated with his name. In 1875 Fischer showed that two salts arise from the diazotised base and neutral potassium sulphite, namely,



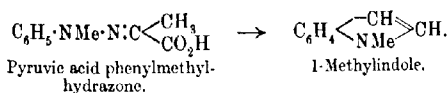
The latter was identical with Strecker's, and Fischer carried the inquiry to another stage by acting on it with benzoyl chloride, producing a substance (dibenzoylphenylhydrazine) which gave benzoic acid and phenylhydrazine hydrochloride when heated with hydrochloric acid; in this manner, phenylhydrazine itself was first obtained as an oil, which ultimately became solid. Later in the same year he simplified the preparation of the base by adding excess of sodium sulphite to benzenediazonium chloride, completing the reduction by means of zinc dust and hydrolysing the phenylhydrazinosulphonate with hot hydrochloric acid. Extending the process to diazotised sulphanilic acid, he prepared phenylhydrazine-sulphonic acid, which had been actually obtained by Strecker and Römer (1871), because in this case they had heated the initial product with hydrochloric acid to remove excess of alkali sulphite.

Owing to the readiness with which hydrogen replaces the nitroso-group in secondary nitrosoamines, attempts by other chemists to prepare aliphatic hydrazines had failed. Fischer succeeded in reducing nitrosodimethylamine to dimethylhydrazine, and, having prepared diethylhydrazine and phenylethylhydrazine, he represented the primary hydrazine derivative by the formula



At the beginning of 1876 he described ethylhydrazine, which arose from hydrolysing diethylsemicarbazide, and expressed the intention of applying this process to the production of hydrazine itself. Throughout this and the succeeding year the simpler changes undergone by phenylhydrazine were studied, and it is noteworthy that at this period Fischer preferred the Kekulé formula for diazonium salts; he had regenerated potassium phenylhydrazino-sulphonate from phenylhydrazine and potassium pyrosulphate, and, converting it by oxidation into the diazonium sulphite, was so impressed by the close experimental relationship between the two substances as to consider this an obstacle to the Strecker formula.

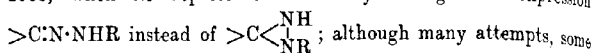
A survey of these early papers indicates the curious fact that although the power of phenylhydrazine to combine with aldehydes was quickly observed by Fischer, he does not appear to have recognised its tremendous value as a general agent for the carbonyl group until nearly ten years after discovering the base. This is probably due to the distraction offered by rosaniline (see below) and minor investigations, by his translation from Munich to Erlangen, and by the work on caffeine (1881), which was destined to lead him to the classification of purine derivatives. It is true that the action of acetaldehyde, benzaldehyde, and furfural had been noted, but it was probably the formation of the sparingly soluble and beautifully crystalline phenylhydrazone of pyruvic acid (1883) which revived the interest in his original discovery. The outstanding feature of 1884, an extraordinarily fruitful year, is the application of phenylhydrazine to carbonyl compounds in general, and the sugar group in particular. In that year, also, he explained the first transformation of a phenylhydrazone into an indole,



induced by the action of hydrochloric acid, and he re-assembled the evidence supporting his constitutional formula for phenylhydrazine, Erlenmeyer having advocated the alternative expression  $\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{NH}$ .



Another interesting point in the early history of the phenylhydrazones is that the name for these important products of condensation does not appear to have been introduced by Fischer until 1888, when he represented them by the general expression

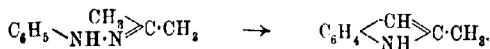


although many attempts, some of which are quite recent, have been made to resuscitate the cycloid representation, Fischer did not take part in the discussions, and the balance of evidence in favour of his formula preponderates.

Even forty years ago, when the boundaries of organic chemistry were comparatively limited, the discovery of an entirely new class of highly reactive compounds by a novice must have been recognised as a portent; but the hydrazines were not the only subject with which Fischer's name came to be associated in the text-books with respect to work accomplished before he was twenty-five years of age. While in Munich he began collaboration with Otto Fischer, and in 1876 the cousins published their first joint paper on the rosaniline bases, obtaining from diazotised leucaniline the hydrocarbon,  $\text{C}_{20}\text{H}_{14}$ , melting at  $58^\circ$ . These experiments were made with the commercial product, and, on repeating them with the dye prepared from purified *p*-toluidine and aniline, they showed in 1878 that the corresponding leuco-base gives triphenylmethane,  $\text{C}_{19}\text{H}_{16}$ , melting at  $93^\circ$ , as recorded by Kekulé, Franchimont, and Hemilian. In view of its production from *p*-toluidine, the dye was named, somewhat unfortunately, "pararosaniline," and they proceeded to regenerate it from triphenylmethane by reducing Hemilian's trinitro-derivative and oxidising the paraleucaniline thus obtained. They concluded (1) that the rosanilines producible from aniline and the toluidines are homologues, of which the simplest, pararosaniline, has the composition  $\text{C}_{19}\text{H}_{17}\text{N}_3$ , whilst commercial fuchsine is a mixture, of which the principal constituent has the formula  $\text{C}_{21}\text{H}_{19}\text{N}_3$ , assigned by Hofmann, and (2) that the parent hydrocarbon of the whole group is triphenylmethane, of which, or of its homologues, the various leucanilines are triamino-derivatives.

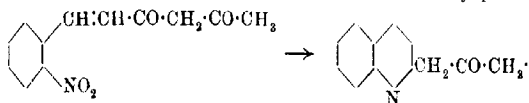
Before proceeding to review the special branches with which Fischer's name is most conspicuously linked, it will be convenient here to notice a few developments of his earlier experiments which are not appropriately included in the following sections. For example, the conversion of suitable phenylhydrazones into derivatives of indole was extended in 1886, when it was found that anhydrous zinc chloride so greatly facilitates the removal of ammonia that the condensation products of primary and secondary arylhydrazines with all saturated ketones or ketonic acids con-

taining the methyl or methylene group adjacent to carbonyl can be transformed into the corresponding indole derivatives by loss of ammonia; as an illustration, acetonephenylhydrazone gives 2-methylindole,

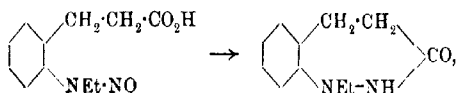


A similar change proceeds with phenylhydrazones of aldehydes containing the methylene group next to the aldo-nucleus, and dimethylindole, methylethyl-, phenylmethyl-, and phenylscatole, together with indolecarboxylic, dimethylindoleacetic, and dimethylindolecarboxylic acids, were prepared.

Other examples of ring-formation were brought to light by Fischer. In 1883 he found that benzoylacetone is produced by hydrolysing benzoylacetate ester, and, utilising this reaction to prepare *o*-nitrocinnamylacetone, he reduced this to acetonylquinoline,



Furthermore, nitrosoethylaminohydrocinnamic acid gave ethylhydrocarbazostyryl,



whilst phenylpyrazoline,  $\text{C}_6\text{H}_5 \cdot \text{N} \begin{array}{c} \text{N} = \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , was obtained in 1887 from the phenylhydrazone of acrolein by the action of dilute sulphuric acid.

#### *Carbohydrates, Glucosides, and Depsides.*

In the year 1886, chemists recognised two aldohexoses (glucose and galactose), two ketohexoses (fructose and sorbose), and one aldopentose (arabinose); three hexobioses (sucrose, lactose, and maltose) were also known to be definite individuals, and one hexotriose (raffinose). The general structure of glucose and galactose as that of straight-chain pentahydroxyaldehydes, and of fructose as a pentahydroxyketone, also unbranched, had been determined by the work of Kiliani, who relegated to its proper position as a tetrahydroxyaldehyde the pentose, arabinose, erroneously classified by its discoverer as an isomeride of glucose. In these few lines may

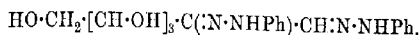
be summarised the exact knowledge of crystalline carbohydrates at the time when Emil Fischer approached the subject, and a true measure of the character and magnitude of his constructive achievement may be gained by comparing the foregoing synopsis with the modern classification of the hexose group as represented by projection formulæ.

From that classification it is seen that amongst the sixteen optically active aldohexoses theoretically realisable, twelve have been either synthesised or configurated, or both, by Fischer and his collaborators. His work on ribose made it possible to include *d*-allose and *d*-altrose in the list, of which there thus remain only the *l*-forms of these two aldoses unknown. It involves also the statement that six amongst the eight possible *dl*-aldohexoses have been realised, whence it follows that *l*- and *dl*-allose with *l*- and *dl*-altrose are the only missing members of the twenty-four optical isomerides comprised in the category.

Highly as this admirable web of theory and practice must be valued, its description is not a complete estimate of his finished contribution to aldohexose chemistry. The foregoing computation of possibilities takes no account of the oxide rings now accepted amongst members of this class. His discovery of  $\gamma$ -methylglucoside, and the consequent recognition of cyclic relations distinct from that occurring in  $\alpha$ - and  $\beta$  glucose, have opened the way to a multitude of contingent isomerides, those of *d*-glucose alone numbering ten. Thus Fischer not only elaborated his own sugar chemistry, but he added to this the foundation of a new carbohydrate classification, the development of which will continue to inspire the prosecution of inquiry by generations following his epoch.

The instrument which enabled Fischer to bend his experimental deftness and his theoretical penetration to the purpose of elaborating so delicate a structure was phenylhydrazine. In 1884 he found that with this agent glucose and fructose yield phenylglucosazone,  $C_{15}H_{22}O_4N_4$ , whilst an isomeride arises from galactose; under similar conditions, maltose and lactose resemble the hexoses, forming individual isomeric osazones,  $C_{34}H_{52}O_9N_4$ , whilst sucrose, at first indifferent, gradually undergoes partial hydrolysis, generating phenylglucosazone from the products of inversion. Closer study showed that this reaction has the peculiarity of presenting a fully hydrogenised compound, phenylhydrazine, in the light of an oxidising (dehydrogenising) agent. The first product is the phenylhydrazone, which, owing to structural difference between glucose and fructose, is not the same from both sugars; a second molecule

of phenylhydrazine now removes hydrogen from the two phenylhydrazones, yielding two structurally different phenylhydrazones of glucosone, which then undergo condensation with a third molecule of phenylhydrazine to produce the osazone,

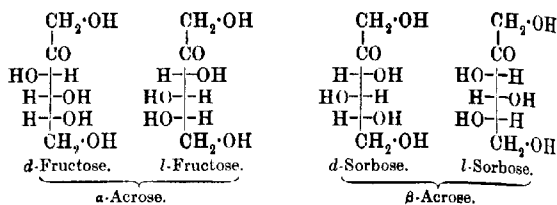


common to both.

The extension of this reaction to all aldoses and ketoses, the formation of phenylhydrazides from sugar-acids, and the analogous application of substituted phenylhydrazines, have rendered invaluable service in the identification and isolation of carbohydrates in general, because although the latter, when crystalline, are quite definite in purified form, they are amongst the most difficult materials to manipulate, on account of their tendency to remain as a syrup in mixtures.

Even more important, though less immediately obvious, has been the operation of this process in a synthetical direction. The aspiration artificially to produce grape-sugar is coeval with organic chemistry itself. Liebig had indicated the fascination of this problem, but the first practical step was taken in 1861 by Butlerow, whose methylenitan was a sweet, pale yellow syrup responding to common tests for glucose, but optically inactive and unfermentable by yeast. He polymerised trioxymethylene with hot lime-water, and twenty-five years later Loew, having conveniently modified Hofmann's method of preparing formaldehyde, subjected this compound to the action of cold lime-water, thus producing a syrup which he called formose. In 1888, by means of phenylhydrazine, Fischer showed that formose is a mixture of at least three aldehydic or ketonic polyhydric alcohols, of which one has the composition  $\text{C}_6\text{H}_{12}\text{O}_6$ , and yields a normal osazone,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$ , also producible from methylenitan.

Fischer himself has stated that the directive influence on his work amongst carbohydrates was the discovery of  $\alpha$ - and  $\beta$ -acrose. In 1887, associated with Tafel, he obtained from acrolein dibromide and baryta a syrup which yielded two osazones, isomeric with one another and with phenylglucosazone. These were called  $\alpha$ - and  $\beta$ -phenylacrosazone, corresponding to the two synthetical sugars  $\alpha$ - and  $\beta$ -acrose, having the composition  $\text{C}_6\text{H}_{12}\text{O}_6$ . The former sugar he subsequently identified with *dl*-fructose, whilst  $\beta$ -acrose, which he suggested resembled sorbose, has been since recognised as the *dl*-form of that ketose (E. Schmitz, 1913). Thus was accomplished the first definite synthesis, in their *dl*-modifications, of the naturally occurring sugars, fructose and sorbose,

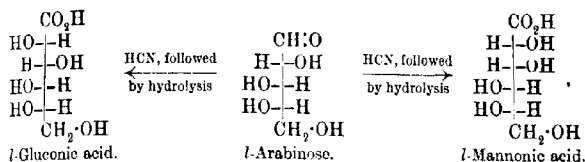


Great as was the advance represented by the acrosazones, the following step might well have daunted a less tenacious investigator. The acroses are optically inactive, and although reducible by sodium amalgam to hexahydric alcohols, of which  $\alpha$ -acritol appeared, and was afterwards shown, to be identical with *d*-mannitol, only 0.2 gram of  $\alpha$ -acritol was obtainable from 1 kilo-gram of glycerol. Use had to be made, therefore, of another reaction, also very tedious experimentally, arising from the study of phenylglucosazone. When this compound is treated with hydrochloric acid, it is hydrolysed completely, leaving the tetrahydroxy-ketonic aldehyde, glucosone; on reducing this product incompletely with zinc dust in acetic acid, the aldehydic group is hydrogenised selectively before the ketonic, yielding fructose. By applying this process to  $\alpha$ -acrosazone, in combination at subsequent stages with Pasteur's methods of separating optical antipodes, the passage from inactive synthetic  $\alpha$ -acrose to sugars identical in all respects with *d*-glucose, *d*-fructose, and *d*-mannose was ultimately effected in the following sequence:  $\alpha$ -acrose  $\rightarrow$  *dl*-glucosazone  $\rightarrow$  *dl*-glucosone  $\rightarrow$  *dl*-fructose ( $\rightarrow$  *l*-fructose)  $\rightarrow$  *dl*-mannitol  $\rightarrow$  *dl*-mannose  $\rightarrow$  *dl*-mannonic acid  $\rightarrow$  *d*-mannonic acid ( $\rightarrow$  *d*-gluconic acid  $\rightarrow$  *d*-glucose)  $\rightarrow$  *d*-mannose  $\rightarrow$  *d*-glucosazone  $\rightarrow$  *d*-fructose.

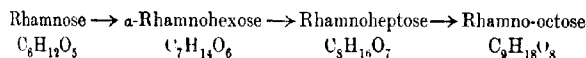
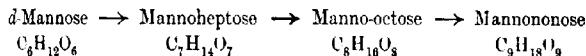
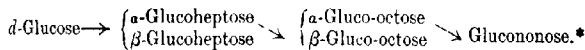
One step in the above series, namely, the conversion of *d*-mannonic acid into *d*-gluconic acid, deserves attention, because the principle underlying it has been, in Fischer's hands, one of the most fruitful devices in the construction and configuration of new sugars, especially in association with the cyanohydrin synthesis and the reduction of polyhydroxylactones to the aldoses themselves. In 1890 he found that gluconic and mannonic acids are interconvertible, an equilibrium mixture of the two being produced when either is heated with quinoline at 140°. This was a far-reaching discovery, because it afterwards appeared that when any monobasic sugar-acid is heated with quinoline or pyridine, the configuration of the carbon atom adjacent to the carboxylic group becomes inverted or epimerised; gluconic and mannonic acids are consequently said to be epimeric. It was this principle, followed by reducing the lactones of the resulting acids, which enabled

Fischer to produce the artificial sugars *l*-glucose, *d*-talose, and *d*-idose through *l*-mannonic, *d*-galactonic, and *d*-gulonic acids, respectively, and the aldopentoses *l*-ribose and *d*-lyxose through *l*-arabonic and *l*-xylonic acids, respectively.

The cyanohydrin reaction, although actually devised by Kiliani (1885), was widely applied by Fischer, who regarded it as a great advance in the study of the sugar group. A typical example of its application is the conversion (1891) of *l*-arabinose, the dextro-rotatory pentose derived from cherry-gum, into *l*-mannonic and *l*-gluconic acids,



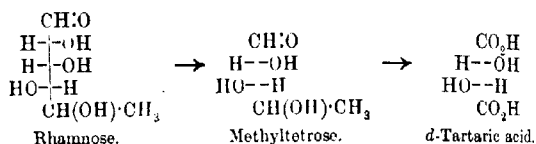
This opened a way to the artificial *l*-glucose and *l*-mannose, whilst a similar transformation of *d*-xylose (at that time known as *l*-xylose), the pentose from wood-gum and oat straw, gave *l*-gulose along with *l*-idose. The method was found to be capable of wide extension, and is limited only by the diminishing amount of material available for each succeeding step; thus, the following series were realised by Fischer:



In 1891 an attack was made on the complex problem of configuration, the system of which it has been necessary to assume hitherto in order to give a coherent synopsis within reasonable limits of space. Fischer's procedure was based on the requirements of van't Hoff's theory, from which it follows that the pentahydroxy-aldehyde of an unbranched carbon chain, in which five carbon atoms are each associated with one hydroxyl group, should appear in sixteen stereoisomeric forms, eight of these being enantiomorphs of the remainder. The projection formulæ of the sixteen possible aldohexoses are then assembled in conjunction with the eight possible aldopentoses, thus indicating the trihydroxyglutaric acids

\* Subsequently extended to glucodecose by Philippe (1911).

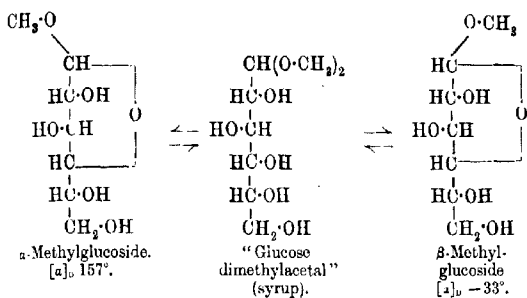
derivable from the latter, the tetrahydroxyadipic acids corresponding with the former, and the structurally symmetrical pentitols and hexitols. Recalling that (1) the cyanohydrin synthesis relates glucose to arabinose, and gulose to xylose, (2) the trihydroxy-glutaric acid from xylose is internally compensated, whilst the isomeride from arabinose is optically active, and that (3) saccharic acid arises from both glucose and gulose, but not from any other hexose, it is possible by a process of considered elimination to limit the representation of *d*- and *l*-saccharic acids to two configurations, which are enantiomorphous, leaving the final selection arbitrary. The choice made by Fischer was a happy one, for he was able finally to confirm it in 1896. Having previously (1894) established the configuration of the three carbon atoms proceeding from the aldehydic group in rhamnose, he degraded the sugar by Wohl's method to the corresponding methyltetrose; oxidation of this yielded *d*-tartaric acid, the configuration of which is thus determined:



Just as the internally compensated mucic acid yields, by equally probable disruptions, *dl*-tartaric acid, so saccharic acid, and hence glucose, yield *d*-tartaric acid, thus providing the keystone for Fischer's configurational system.

Although it still simplifies discussion of the aldohexoses to represent them as containing a free aldehydic group, many years have elapsed since this view of their structure was modified. Amongst the earliest known compounds of organic origin are the glucosides, for example, amygdalin, indican, salicin, and myronic acid, owing their class-name to the production of glucose on hydrolysis, which led to their being regarded as ethereal derivatives of this or a related sugar. In 1893 Fischer found that under the influence of hydrogen chloride, glucose combines with methyl alcohol to form the simplest of the glucosides, which he called methylglucoside, and the discovery ultimately elucidated the structure of the sugar-like polysaccharides and of glucose itself. He soon showed this method of synthesis to be general with aldoses and ketoses for the one part, and applicable to the alcohols in which they are soluble, for the other; somewhat similar methods lead from acetone and benzaldehyde to the isopropylidene and benzylidene compounds, respectively, products which have been applied to the preparation

of mono-, di-, and tri-methyl derivatives of glucose (Irvine and Scott, 1913). Whilst Fischer indicated the probability of isomerism following the asymmetry of the methoxylated carbon atom, the second methylglucoside was brought to light by van Ekenstein (1894). The mechanism of glucoside formation, in which it seemed convenient to make an arbitrary selection of alternative formulae for the  $\alpha$ - and  $\beta$ -modifications, was then tentatively represented as follows:



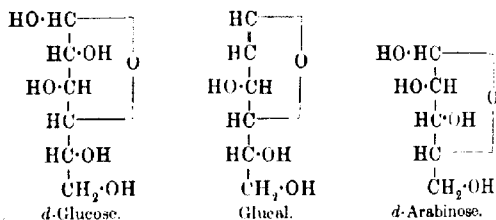
This proposal was in accord with Tollens'  $\gamma$ -oxide (preferably butylene oxide) formula for glucose (1883), and offered a substantial basis for the highly probable explanations, by E. F. Armstrong and by Lowry, of the long observed mutarotation of that sugar. The isolation of glucose in a second form was achieved by Tanret (1896), and it was subsequently accepted that  $\alpha$ -glucose, with  $[\alpha]_D 110^\circ$ , and  $\beta$ -glucose, with  $[\alpha]_D 19^\circ$ , pass, on dissolution in water, to an equilibrium mixture having  $[\alpha]_D 52.5^\circ$ . Simon's view (1901) of  $\alpha$ - and  $\beta$ -glucose as lower homologues of  $\alpha$ - and  $\beta$ -methylglucoside, respectively, has been confirmed by E. F. Armstrong (1903), who correlated each methylglucoside with its parent glucose through the agency of an appropriate enzyme.

There the question remained during the next ten years, when the seed of revolution was sown by Fischer himself. In 1914, J. U. Nef, who had been occupied with a protracted survey of the oxidation undergone by sugars in alkaline solution, challenged the foregoing conception of methylglucoside isomerism by claiming this to be structural in place of steric, and representing the  $\beta$ -form of methylglucoside and of penta-acetylglucose as propylene oxides instead of butylene oxides. Strong arguments against this disturbing proposal were brought forward by Fischer, who simultaneously (1914) described a third methylglucoside. The syrupy companion of  $\alpha$ - and  $\beta$ -methylglucoside, hitherto assumed to be the dimethylacetal, was distilled under 0.2 mm. pressure, and



found to be isomeric with them; it resembled them in stability towards alkali and Fehling's solution, but revealed a profound contrast in its behaviour towards acids, which hydrolyse it with extraordinary readiness. Moreover, whilst  $\alpha$ -methylglucoside is hydrolysed by maltase (not by emulsin) and  $\beta$ -methylglucoside is hydrolysed by emulsin (not by maltase),  $\gamma$ -methylglucoside is indifferent to both. Fischer conceded the probability of the new glucoside owing its individuality to another form of oxide ring, and was inclined to regard it as a mixture of two or more such isomerides. Both possibilities have been supported by Irvine, Fyffe, and Hogg (1915) from a study of tetramethyl- $\gamma$ -glucoside and tetramethyl- $\gamma$ -glucose, in which emphasis is laid on the readiness with which it undergoes condensation with acetone and on the instantaneous oxidation of the new methylglucoside by cold alkaline potassium permanganate, an agent which has no effect on the  $\alpha$ - and  $\beta$ -methylglucoside.

This remarkable behaviour towards permanganate invites comparison between the derivatives of  $\gamma$ -glucose and glugal, obtained as the triacetyl derivative on reducing  $\beta$ -acetyl bromoglucose (Fischer and Zach, 1913). The conversion of triacetylglugal through the dibromide and the related bromohexose into phenylglucosazone, and the oxidation by ozone to triacetyl-*d*-arabinose (posthumous publication with Bergmann and Schotte, 1920), indicate the first and second carbon atoms as participants in the double linkage of glugal, the relationship of which to *d*-glucose and *d*-arabinose is consequently represented as follows:

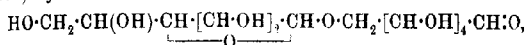


Glugal is thus a derivative of dihydrofuran, and gains piquancy from having beguiled Fischer into using rare words of enthusiasm when describing its production, which, he declared, "vom Standpunkt der Strukturchemie betrachtet, einer der merkwürdigsten Vorgänge ist, die man bisher in der Zuckergruppe kennen gelernt hat. Sie beweist von neuen, welch wunderbarer Stoff der Traubenzucker ist."

Although Fischer did not commit himself to the particular form of oxide represented by  $\gamma$ -glucose, which has not yet been isolated,

a point has been reached which indicates an ethylene oxide-ring structure for this compound. Before passing to the next branch of the subject, it should be mentioned that the experiments of Böeseken (1913) on the conductivity of boric acid as influenced by polyhydroxy-compounds have thrown some doubt on the accepted configuration of the  $\alpha$ - and  $\beta$ -methylglucoside, in which, according to his deductions, the relative positions of the terminal methoxy-group and hydrogen atom should be inverted, and the corresponding rearrangement made in  $\alpha$ - and  $\beta$ -glucose.

In conformity with his observations on artificial glucosides, Fischer represented the disaccharides as hexosides composed of the hexoses into which they are resolved by acids or enzymes, one hexose molecule playing the part of the methyl group in the less complex derivatives. Thus maltose and lactose were represented (1893) by the structural formula



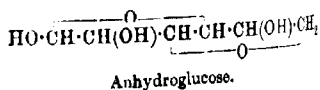
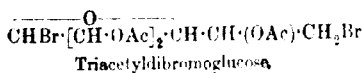
of which the left-hand portion stands for glucose in maltose and for galactose in lactose, whilst the remainder is glucose in both. Moreover, the relationship to the methylglucosides was shown (1894) by their behaviour towards emulsin, which hydrolyses lactose (glucose- $\beta$ -galactoside) and is without action on maltose (glucose- $\alpha$ -glucoside). Structurally, this agrees with the oxidation of lactose to the monobasic lactobionic acid,  $\text{C}_{12}\text{H}_{22}\text{O}_{12}$ , and of maltose to the isomeric maltobionic acid (1889), which on hydrolysis yield galactose and glucose, respectively, associated in each case with gluconic acid; moreover, lactosecarboxylic and maltosecarboxylic acids, obtained from the respective disaccharide by the cyanohydrin reaction, yield the above-mentioned hexoses in company with  $\alpha$ -glucoheptonic acid when hydrolysed.

Sucrose (cane-sugar), being devoid of aldehydic or ketonic attributes, is at once a fructoside and a glucoside. Fischer's formula (1893), based on that conception, remained unchallenged until his isolation of  $\gamma$ -methylglucoside, when he drew attention to the similar behaviour of these two substances towards acids. Whilst it is assured that the glucose residue has the same type of oxide ring as that of the  $\alpha$ - and  $\beta$ -glucosides, his inference that the fructose component is in the  $\gamma$ -form (that is, an ethylene oxide) is supported by Haworth and Law (1916), who adduced new arguments in favour of representing sucrose by a formula in accordance therewith, subsequently confirming (1919) Fischer's original representation of maltose, in which the free aldehydic group is modified to the now conventional butylene oxide. By application of the methylation process, with which the St. Andrews laboratory has

been so conspicuously associated, Haworth (1918) was led to refer Fischer's modified lactose formula (1893) to melibiose.

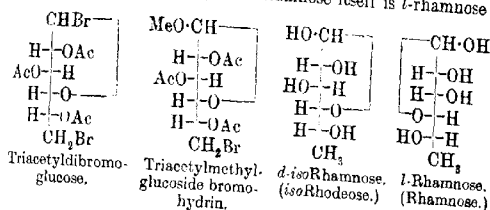
With so constructive a mind and an armoury of synthetical method so full of weapons, the magnetic problem of elaborating polysaccharide molecules was not likely to be neglected by Fischer. The individuality of *isomaltose*, produced by the action of cold fuming hydrochloric acid on glucose (1890 and 1895), was actively criticised; indeed, it was shown later by E. F. Armstrong that although *isomaltose* is formed in this process, it is accompanied by maltose. Subsequent attempts, however, were based on unassailable foundations. The first of these, in association with E. F. Armstrong (1902), depends on the action of  $\beta$ -acetylchloroglucose on the sodium derivative of galactose, and of  $\beta$ -acetylchlorogalactose on the sodium derivatives of glucose and galactose, the resulting disaccharides forming osazones. The galactosidoglucose closely resembled melibiose in its behaviour towards enzymes and the less delicate chemical agents, but the glucosidogalactose was distinct from lactose; all three resembled the  $\beta$ -glucosides in being hydrolysed by emulsin. From  $\beta$ -acetylbromoglucose and silver carbonate there was produced the octa-acetyl derivative of a disaccharide called *isotrehalose* (Fischer and Delbrück, 1909) from its close resemblance to the carbohydrate which is found in many fungi and which appears to play in these the part of sucrose in chlorophyllaceous and starch-bearing plants; application of this method to acetylbromolactose gave distinct evidence of a tetrasaccharide being formed (1910), but this compound was not defined.

The group of acetyl-halogen derivatives, typical members of which are involved in the reactions just described, was destined to perform important service in Fischer's later work. When the action of hydrogen bromide on penta-acetylglucose is protracted beyond the period required for conversion into tetra-acetylbromoglucose, a second acetoxy-group is displaced by bromine, and  $\beta$ -tri-acetyldibromoglucose arises (Fischer and E. F. Armstrong, 1902). Exchange of one halogen atom for the methoxy-group leads to triacetylmethylglucoside bromohydrin, converted by warm baryta into the anhydromethylglucoside,  $C_7H_{12}O_5$ , which is hydrolysed by acids to anhydroglucose (Fischer and Zach, 1912):



This is crystalline, produces colour in Schiff's reagent, and forms crystalline derivatives with phenylhydrazine, whilst reduction with sodium amalgam gives anhydrosorbitol; anhydrogluconic acid follows oxidation by bromine.

The result of reducing triacetylmethylglucoside bromohydrin is noteworthy also, because it enabled Fischer to elucidate the configuration of the undetermined carbon atom in rhamnose (1912). With Zach, he found that replacement of bromine by hydrogen gave a triacetylmethylglucoside, leading to a methylpentose on complete hydrolysis, proving that the bromine atom in triacetylmethylglucoside bromohydrin occupies the terminal position in the chain. It was further discovered that the new methylpentose is the optical antipode of isorhamnose, which is related to *d*-glucose as is rhamnose to *l*-mannose; thus rhamnose itself is *l*-rhamnose:



Another remarkable application of acetylbromoglucose led to the synthesis of mandelonitrile-glucoside, which had been obtained by Fischer (1895) as a crystalline, levorotatory, non-reducing product of hydrolysing with yeast-maltase the disaccharide group in amygdalin without severing the connexion between mandelonitrile and the residual hexose; subsequently, two isomerides were isolated, namely, sambunigrin from the leaves of *Sambucus niger* by Bourquelot and Danjou (1905), and prulaurasin from *Prunus laurocerasus* by Hérissé (1906). Caldwell and Courtauld (1907) recognised all three as  $\beta$ -glucosides, Fischer's being *l*-mandelonitrile- $\beta$ -glucoside; they regarded sambunigrin as *d*-mandelonitrile- $\beta$ -glucoside and prulaurasin as the *dl*-form. This forecast was confirmed by the synthesis (Fischer and Bergmann, 1917), which followed the action of silver carbonate on acetylbromoglucose in molten ethyl *dl*-mandelate, the product giving *dl*-mandelamide-glucoside with methyl-alcoholic ammonia; dehydration following resolution gives the mandelonitrile-glucoside in both active forms. It is to be regretted that Fischer himself did not survive to extend this process to the synthesis of amygdalin, which, in 1895, he believed to be "ein Derivat der Maltose oder einer ganz ähnlich construirten Diglucose." One of his last papers, however, describes

the synthesis of glycollonitrile-glucoside (1919), the simplest of the cyanogenetic glucosides, immediately following that of linamarin (from flax), the glucoside of acetonecyanhydrin.

Recalling the manifold parts played by the substituted amino-group in animal and vegetable metabolism, it is a singular fact that so few amino-derivatives of a glucose type have been encountered amongst the products. It was natural, therefore, that glucosamine, isolated from lobster shells by Ledderhose (1878), should attract Fischer's attention, because its empirical relationship to glucose is expressed by a simple interchange of hydroxy- and amino-groups; the actual connexion, however, is elusive, for whilst indirect processes of replacement (Irvine and Hynd) lead variously to *d*-glucose (1912) and *d*-mannose (1914), thus pointing to a Walden inversion, the direct action of nitrous acid involves dehydration in addition to the normal exchange.

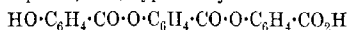
The component of lobster shells which yields glucosamine having been called chitin, the sugar-like product,  $C_6H_{10}O_5$ , from the base and nitrous acid was called chitose; this was oxidised to chitonic acid,  $C_6H_{10}O_6$ , by Fischer and Tiemann (1894). By the same change they related glucosamine itself to chitamic acid, this being synthesised from *d*-arabinose (1903) by Fischer and Leuchs, who then reduced it to *d*-glucosamine; later in the same year Fischer and Andreae connected chitose and chitonic acid experimentally

with hydroxymethylpyromucic acid, 
$$\begin{array}{c} \text{CH-CH} \\ | \quad | \\ \text{HO-CH}_2\text{-C}\cdot\text{O-CH}\cdot\text{CO}_2\text{H} \end{array}$$
 to which is also related chitaric acid, the product from chitamic (glucosamic) and nitrous acids. Thus chitose, whether regarded as an aldehyde or a butylene oxide, is derived from tetrahydrofuran.

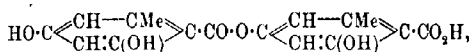
The triacetylmethylglucoside bromohydrin already mentioned was utilised by Fischer in relation to glucosamine. With Zach (1911) he found that ammonia converts it into a  $\beta$ -methylglucoside, in which the amino-group has replaced hydroxyl; but hydrolysis, instead of producing glucosamine, led to an isomeride. It has to be admitted that this branch of sugar chemistry retains a somewhat perplexing aspect, to which the loose nomenclature involved in such expressions as "aminoglucose," "aminofructose," and "methylglucosamine" contributes. This is all the more regrettable in view of the great biochemical interest attaching to glucosamine as a connecting link between carbohydrates and amino-acids.

Before closing this chapter, there remains to be described one of the most remarkable achievements in a series unsurpassed by any organic chemist, namely, the synthesis of tannin. In 1908 Fischer required the chloride of chloroacetyltyrosine for the synthesis of glycyltyrosylglycine, and, being embarrassed by the presence of the

phenolic group, protected this, prior to treatment with phosphorus pentachloride, by substituting the methylcarbonato-group for hydrogen. Immediately applying this device to phenolcarboxylic acids, he prepared *p*-hydroxyhippuric acid (the isomeride of allyluric acid) with galloyl-*p*-hydroxybenzoic and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acids. Anhydrides analogous to the last-named were rapidly multiplied, and were named "depsides" by Fischer and Freudenberg (1910), owing to the resemblance which many display towards the tannins; in parallel with the polypeptides and polysaccharides, such compounds may be classified as didepsides, tridepsides, etc., typified by the formulæ



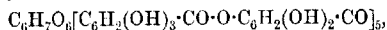
and  $(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O})_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ . The only recognised natural sources of the depsides are the lichens, of which the best known constituent is lecanoric acid, the depside of orsellinic acid, and in conjunction with his son Hermann, Fischer synthesised lecanoric acid (1903), and represented it as the *p*-ester,



of which evernic acid is the *p*-methyl ether.

The history of the tannins dates from the eighteenth century, but from the standpoint of this review the earliest year of importance is 1852, when Strecker deduced the formula  $\text{C}_{27}\text{H}_{22}\text{O}_{17}$  for gallotannic acid or gall-nut tannin, which he regarded as a compound of grape-sugar and gallic acid in the molecular proportion 1:3. For half a century there prevailed a conflict of opinion as to the presence of a glucose residue, the production of sugar on hydrolysis being denied by several chemists, and the proportions in which it was obtained by the followers of Strecker varying much amongst themselves. In consequence of this uncertainty, Schiff's view (1871) of tannin as consisting principally of digallic acid preponderated until recently. The conductivity measurements by Walden (1897), however, paved a way for the unquestionable differentiation of the two materials by Fischer, who synthesised digallic acid in 1908 and found it to be crystalline, although astringent; moreover, in 1912, having adopted a method of purifying the principal constituent of Chinese tannin and of producing specimens having constant optical activity, he and Freudenberg proceeded to show that when hydrolysed with sulphuric acid it yields 7 to 8 per cent. of glucose, an amount which they regarded as probably too low in view of the extended period occupied in completing the operation. They then expressed the opinion that the principal constituent of tannin is not a glucoside, but a sugar

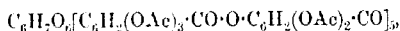
ester comparable with pentabenzoylglucose, in which the acyl group is that of digallic acid. Expressed by the formula



such a compound having the molecular weight 1700 would yield 10.6 per cent. of glucose and 100 per cent. of gallic acid on hydrolysis.

At the time of making this very penetrating speculation, they synthesised pentagalloylglucose, which they found to be a tannin, not identical with gall-nut tannin, but resembling it closely in taste, solubility, amorphism, optical activity, and feeble acidity; moreover, it precipitates gelatin and alkaloids, becomes gelatinous with arsenic acid, and develops colour with ferric chloride. In the course of this investigation they prepared hepta(tribenzoyl-galloyl)-*p*-iodophenylmalto-azone, a freak molecule of gigantic dimensions (M.W. 4021), vastly exceeding those of any other synthetic product.

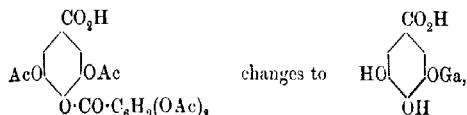
Valuable as the use of methylcarbonato-derivatives had proved, it did not suffice to perfect the aim in view, namely, to synthesise the main principle of Chinese tannin. This was accomplished in 1918, following the observation that the corresponding acetyl compounds are superior to the methylcarbonato-derivatives for depside production. In making this advance, Fischer explained that the acetylated phenolcarboxylic acids would certainly have been used much earlier had not he been misled by the statements of previous workers as to the difficulty of removing the acetyl group, which actually proceeds quite smoothly. The chloride of penta-acetyl-*m*-gallic acid, unlike the methylcarbonato-derivative, is crystalline, and with  $\beta$ -glucose yields the compound,



which is deacetylated by cold aqueous sodium hydroxide at  $0^\circ$ , giving penta(*m*-digalloyl)- $\beta$ -glucose (Fischer and Bergmann, 1918). The resemblance between this artificial tannin and the principal constituent of Chinese tannin is much closer than that offered by pentagalloylglucose; the two materials are, in fact, indistinguishable, excepting with respect to optical activity, and the same remark applies to penta(*m*-digalloyl)- $\alpha$ -glucose, the recorded  $[\alpha]_D^{20}$  in water being  $43.8^\circ$  and  $42.3^\circ$  for the derivatives of  $\alpha$ - and  $\beta$ -glucose, respectively, and  $70^\circ$  for the purified Chinese tannin. The correspondence between the potassium salts (1919) is even closer, those from Chinese tannin, pentadigalloyl- $\alpha$ -glucose, and pentadigalloyl- $\beta$ -glucose having  $[\alpha]_D^{20}$   $46.3^\circ$ ,  $56.6^\circ$ , and  $33.7^\circ$  respectively.

It is therefore justifiable to claim that gallotannic acid or gall-

nut tannin has been synthesised. Incidentally to this remarkable conclusion, it was observed that when acylated *p*-digallic derivatives are hydrolysed, even by the most delicate methods, the galloyl nucleus is transferred from the para- to a meta-hydroxy-group; for instance, under the influence of alkalis, ammonia, or mineral acids,



and hence penta-acetyl-*p*-digallic acid yields *m*-digallic acid.

Thus was brought to a conclusion, in the closing months of his darkened life, that illustrious chapter of chemistry with which Emil Fischer first drew on himself the admiration of his contemporaries. It represents the fruit of thirty-five years' unremitted labour and the ripening of an intellectual and experimental technique but rarely developed in the history of scientific endeavour. Begun in the vigorous days of his early manhood, when domestic happiness suffused his professional activity and adorned the promise of a brilliant career, it supported him in his first tragedy, stirred to the utmost the deep resources of his mind, and finally solaced those concluding years in which he was compelled to witness the pillars of Prussianism crumbling at the feet of his disillusioned and bewildered countrymen.

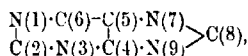
#### *Purine Derivatives.*

Some of the most notable figures in chemical history have devoted themselves to the problems which cluster round uric acid and its allies. Scheele, Bergmann, Fourcroy, Prout, Liebig, Mitscherlich, Wöhler, von Baeyer, Strecker, Stenhouse, and Gerhardt are found in the list of names connected with the subject, and to a high place of honour in this galaxy Fischer is most assuredly entitled. Between 1881, when he resolved caffeine into methylcarbamide and dimethylalloxan, and 1914, the year in which he synthesised a nucleotide in the form of theophylline-*d*-glucosidephosphoric acid, the literature was enriched by a succession of systematic observations which reached a climax in 1898, when he derived purine from uric acid by means of indirect deoxidation.

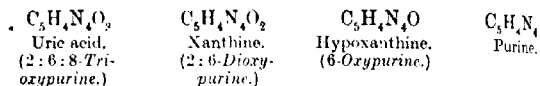
Although uric acid was discovered in 1776, fifty-eight years elapsed before its composition was established, and four years later, in 1838, Liebig and Wöhler published their comprehensive survey of its oxidation products; the true nature and significance of these



were revealed by von Baeyer's experiments, described in 1863 and 1864, thus preparing the ground for the now accepted constitutional formula proposed by Medicus in 1875. This was confirmed in 1888 by Behrend and Roosen, whose synthesis of uric acid, unlike its predecessors, was achieved by definite steps, a feature also of that by Fischer and Ach in 1895. The modern system of notation, according to which the diureides are classified as derivatives of purine and referred to the bicyclic nucleus,

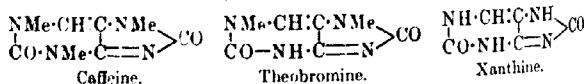


was promulgated by Fischer in 1897, thirteen years after his introduction of the name (*purum:uricum*) in connexion with the methyl derivative. The relationship



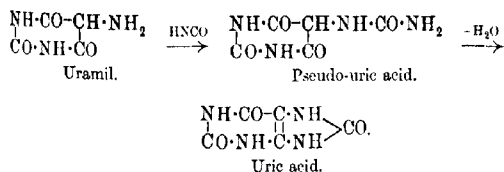
was thus consolidated, the catalogue of purine derivatives contributed by Fischer and his collaborators prior to 1900 embracing upwards of 130 individuals.

The readiness with which caffeine lends itself to experimental treatment led Fischer to open attack on the problem of uric acid by first elucidating the constitution of that base, and a preliminary communication thereon appeared in 1881. His introductory work dealt also with xanthine, theobromine, and guanine. By oxidising aqueous caffeine with chlorine, Rochleder had obtained amalic acid (tetramethylalloxantin), which Fischer showed to be preceded by chlorocaffeine, and to arise from the action of hydrochloric acid on dimethylalloxan; the latter substance and methylcarbamide were found to be the principal products of oxidising caffeine in the manner indicated, and it was proved convenient to prepare chlorocaffeine by acting with the halogen in absence of water. Similarly, theobromine was oxidised to methylcarbamide and methylalloxan, showing that when caffeine is produced by methylating theobromine, the entrant methyl group becomes attached to the alloxan ring. Next, improving the preparation of xanthine from guanine, Fischer oxidised it to alloxan and carbamide, and by acting on the lead derivative with methyl iodide obtained theobromine; on the basis of these and subsidiary experiments, he assigned the following constitutional formulæ (see, however, later):



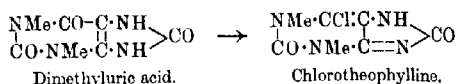
It is noteworthy that even at this period (1882) the products interested him from the standpoint of relation between chemical constitution and physiological action; moreover, Dr. Ludwig Knorr is mentioned as his assistant.

In 1864 Strecker stated that Rheineck had reduced uric acid to xanthine and sarcine (hypoxanthine) by means of sodium amalgam, but he never mentioned the subject again, and did not include the observation in his "Lehrbuch." Fischer found that uric acid is not changed by sodium amalgam, and likewise that, contrary to the statement of Kossel, hypoxanthine is not converted into xanthine by nitric acid. Thus in 1884, uric acid, xanthine, and hypoxanthine, so similar in origin, behaviour, and composition, had no direct experimental connexion with one another. In that year Fischer studied methyluric acid in the hope of establishing the foregoing relationship with respect to the methyl derivatives of xanthine and hypoxanthine. To the existing compound, which gives carbamide and methylalloxan on oxidation, he added an isomeride, which yields methylcarbamide and alloxan when oxidised, and is converted by phosphorus pentachloride into trichloromethylpurine, from which methyluric acid can be regenerated. Complementary also to the dimethyluric acid, which gives methylcarbamide and methylalloxan when oxidised, he discovered an isomeric dimethyl derivative yielding cholestrophan (dimethylparabanic acid). It was thus established that, in addition to the ring which appears in the form of alloxan (mesoxalylcarbamide), uric acid contains two imino-groups associated with one another as in carbamide itself. The methylation of uric acid was then carried to the trimethyl derivative, apparently isomeric with hydroxycaffeine (see later), and to tetramethyluric acid, isomeric with methoxycaffeine, but having all the methyl groups attached to nitrogen, thus indicating the presence of four imino-groups in uric acid, as required by the structural formula previously advanced by Medicus. This was further confirmed in 1895, when Fischer and L. Ach added the final step in the transformation,



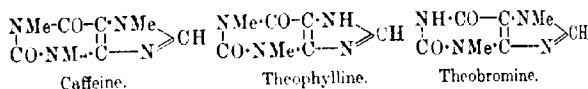
Then, applying this process to dimethylpseudo-uric acid, they produced a third dimethyluric acid, convertible by phosphorus penta-

chloride into chlorotheophylline, from which theophylline arises on exchanging halogen for hydrogen:



This completed the synthesis of theophylline, and, incidentally, of caffeine.

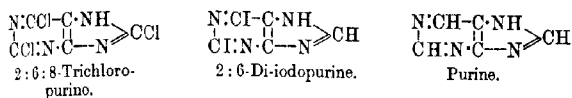
Then arose a situation which is rarely encountered in the course of Fischer's investigations. He was compelled by his own experiments to revise the structural formulæ which he had assigned to xanthine and its derivatives, caffeine, theobromine, and theophylline. In 1895 he had produced a fourth dimethyluric acid by exchanging halogen for hydroxyl in bromotheobromine, and the simplicity of this procedure did not harmonise with the profound structural rearrangement apparently involved. A more rigid examination of hydroxycaffeine, believed to be isomeric with trimethyluric acid, showed it to be identical with that substance, and by varying the conditions of methylation, tetramethyluric acid was obtained from it. Moreover, hydroxycaffeine was produced without difficulty from the corresponding trimethyl*pseudouric* acid, and finally by direct methylation of uric acid itself. In consequence of these discoveries, Fischer modified his previous expressions and assigned the following in 1897:



During his investigation of methyluric acid in 1884, Fischer had found that phosphorus pentachloride in presence of the oxychloride easily replaces two, and finally all three, oxygen atoms by chlorine, producing trichloromethylpurine. In 1897, assisted by L. Ach, he converted uric acid by the same process into 8-oxy-2,6-dichloropurine, reducible to 8-oxypurine isomeric with hypoxanthine, and convertible by ammonia into 6-amino-8-oxy-2-chloropurine; this was reduced to 6-amino-8-oxypurine isomeric with guanine, from which nitrous acid produced 6:8-dioxypurine isomeric with xanthine. The complete replacement of oxygen by chlorine was much more difficult, but by heating 8-oxy-2,6-dichloropurine with seventy parts of phosphorus oxychloride at 150°, Fischer obtained trichloropurine, a basic substance giving the 7- and 9-methyltrichloropurines on methylation, and providing him with material for completing the synthesis of hypoxanthine

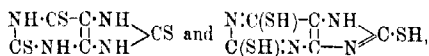
(6-oxypurine), xanthine (2:6-dioxypurine), adenine (6-amino-purine), and guanine (2-amino-6-oxypurine).

The goal towards which Fischer first directed himself in 1884 was now reached. Purine, the parent of the group, and on which the nomenclature and notation of the whole series had been based, lay open to isolation; the accomplished facts were described in 1898. Trichloropurine was reduced in two stages, the first depending on the action of hydrogen and phosphonium iodides at 0° and producing 2:6-di-iodopurine, from which purine itself was obtained by the action of zinc on a boiling aqueous solution:



Purine was thus found to be a definite entity, amphoteric in character and harmonising completely with its position in the series.

Attention has been drawn to the difficulty with which uric acid is converted into trichloropurine, and to the fact that only one halogen atom in this compound is exchanged for oxygen by alkali hydroxides. Alkali sulphides, however, rapidly displace all three, producing triithiopurine (1898), and of the two tautomeric formulæ,



Fischer preferred the latter. Another by-path was pursued in 1900, when he prepared 9-phenyluric acid from the corresponding phenylpseudouric acid, which results from the action of phenyl-carbimide on uramil; this was followed by 9-phenylpurine.

The series of six dimethyluric and four trimethyluric acids was completed with assistance from F. Ach by the preparation of 1:9-dimethyl- and 1:7:9-trimethyluric acids, but the monomethyl derivatives presented a curious anomaly. According to the lactame formula for uric acid, there should be four methyluric acids, in which the alkyl group occupies the position 1, 3, 7, or 9 respectively, but the existence of two additional ones was claimed. Of these six methyluric acids, Fischer and F. Ach (1899) showed that three appear to have the alkyl group attached to the same nitrogen atom, numbered 3 in the purine nucleus, giving the same methylallantoin (on oxidation) and tetramethyluric acid. The mystery remained unsolved until 1916, when an independent examination of the materials by Biilmann and Bjerrum, Biltz and Heyn, showed that the supposed difference is due to the contamination of

3-methyluric acid with a varying proportion of the 9-methyluric acid.

Although for many years displaced from his experimental attention, the purines became involved in Fischer's synthesis of nucleotides. It has already been seen that acetylbromoglucose is a valuable agent in elaborating glucosides, and in 1914, assisted by B. Helferich, he brought this compound into action with the silver derivative of numerous oxypurines, producing the *d*-glucosides of theophylline, theobromine, adenine, hypoxanthine, and guanine; the outstanding feature of these compounds is the readiness with which they are hydrolysed, thus being distinguished from derivatives of glucosamine. Finally, by adding a cold mixture of phosphoryl chloride and pyridine to a solution of theophylline-*d*-glucoside in pyridine, he prepared, later in the same year, theophylline-*d*-glucosidephosphoric acid, the first synthetic nucleotide.

#### *Amino-acids, Polypeptides, and Proteins.*

In view of their extent and the far-reaching biochemical conclusions which have been based on them, the labours of Emil Fischer in the region of proteins will make the same appeal to the imagination and evoke the same delight in craftsmanship as his activities amongst carbohydrates. Owing to the much greater complexity of the subject, however, the intrinsic results may at first appear less complete; but the relative success is equally remarkable, because his treatment of this branch reveals the skilful manipulation of sensitive materials, the deft application of experimental indications, and the constructive diligence in synthetic achievement already so admirably displayed by his earlier work.

The amino-acids bear to the proteins a relationship recalling that of a hexose to a polysaccharide. Accordingly, it was with those materials that Fischer began, in 1899, experiments which were destined to reveal the chemical nature of the proteins themselves, and to furnish material which indicates, at least, the manner in which lifeless protein may ultimately be synthesised. It had then been recognised that nine amino-acids, three diamino-acids, and cystine were obtainable by hydrolytic or enzymic disruption of protein molecules; the synthesis of glycine, alanine,  $\alpha$ -amino-valeric acid, leucine, aspartic acid, glutamic acid, phenylalanine, and tyrosine, all in their *DL*-forms, had been accomplished either by Strecker's method or by substituting the amino-group for halogen in the respective  $\alpha$ -chloro- and  $\alpha$ -bromo-acids, but serine, although discovered in 1865, was not synthesised until 1902 (Fischer

and Leuchs). The resolution of these products into their optically active components had been limited by their amphoteric nature, and was easy only in the case of aspartic acid, Piutti having shown, in 1887, that asparagine is resolved by simple crystallisation from water.

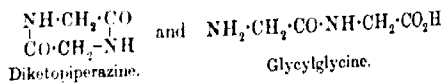
By suppressing the basic aspect of the amino-acids, and thus encouraging their capacity to form recrystallisable salts with the natural alkaloids, strychnine and brucine, Fischer and his collaborators first resolved into their antipodal components the *dl*-forms of alanine,  $\alpha$ -aminobutyric acid, leucine,  $\alpha$ -amino-*n*-caproic acid, phenylalanine, tyrosine, aspartic and glutamic acids, valine, serine, isoserine, and proline. The device by which this was effected consists in benzoylating (1899), formylating (1905), and, in the case of serine, *p*-nitrobenzoylating (1906) the amino-group, resolving the *dl*-acylamino-acid by recrystallising its salts with strychnine or brucine, and hydrolysing separately the antipodal benzoyl, formyl, or *p*-nitrobenzoyl derivative of the *d*- and *l*-amino-acid. In this manner were accumulated, in greater quantity and variety, optically active units, which thus became available as building materials for the construction of polypeptides approaching the peptones in physical characteristics.

The foregoing acyl derivatives, in common with others depending on the reactivity of the amino-group with phenylcarbimide and benzenesulphonyl chloride, are useful for identification as well as isolation of their parent compounds, but some still better for the former purpose followed from combination with  $\beta$ -naphthalenesulphonyl chloride (1902); the resulting derivatives are formed in good yield, are sparingly soluble, and crystallise sufficiently well to facilitate the recognition of hydroxyamino-acids and even polypeptides themselves, in addition to the compounds from which the latter are built. Thus, to a minor extent,  $\beta$ -naphthalenesulphonyl chloride assumes the part played by phenylhydrazine in the sugar group, affording an instrument for isolating freely soluble and elusive substances.

Early attempts to explain the structure of proteins had been hampered by experimental obstacles to the separation of amino-acids produced in such complex mixture by hydrolysis; with the exception of tyrosine and cystine, which are sparingly soluble in water, the major portion of the mixture remains as a syrup after the principal constituent has crystallised. It was thus a practical advance of the first magnitude which Fischer made as the result of his inquiry (1900) into the esters which, owing to the suppression of the carboxylic function, have the properties of aliphatic amines; this feature had been recognised in 1883 by Curtius, whose process

for isolating the esters was modified by Fischer and applied by him to separating the amino-acids in a complex mixture through fractional distillation. The procedure offers considerable experimental difficulty, but it is the only one which has been really successful, and its purpose has now been achieved with a large number of elaborate molecules. Edestin, elastin, fibrin, globin, gluten, keratin, and the albumins of egg, serum, and milk are examples of the zeal with which Abderhalden has pursued this line of inquiry, whilst Osborne and his collaborators, by similar methods have ascertained the component amino-acids of amandin, exoelisin, gliadin, glycinin, hordein, phaseolin, and zein. Particularly to Fischer himself is due the resolution of the fibroin produced by silkworms and spiders, incidentally emphasising the remarkable biological fact that there is only slight chemical difference between the synthetic products of two creatures whose diet is so vastly divergent. He showed (1907) that the silk of the Madagascar spider gives, per cent.: glycine 35.1, *D*-alanine 23.4, *L*-leucine 1.7, *L*-tyrosine 8.2, proline 3.7, *D*-glutamic acid 6.1, diamino-acids (calculated as arginine) 5.2, ammonia 1.1, and fatty acids 0.6; thus the principal difference is the large proportion of glutamic acid, which has not been derived from ordinary silk, and the absence of serine.

Some indication of the nature and variety of the chemical units from which the proteins are constructed having been given, attention must now be directed towards the notable attempts made by Fischer artificially to elaborate protein molecules from their component elements. It is a noteworthy feature of the proteins that, in spite of certain basic properties and the prompt appearance of the amino group on hydrolysis, the amount of nitrogen liberated by nitrous acid is trifling compared with the percentage of that element in the original material. This fact, in conjunction with the early recognition of hippuric acid as benzoylglycine, gives a clue to the manner in which amino acid molecules are associated in the natural products now under consideration, and several observations by the earlier investigators confirm it. The simplest of these is the production of a bimolecular anhydride of glycine by the auto condensation of the ethyl ester (Curtius, 1888). Two such anhydrides are conceivable,

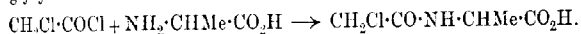


according to the proportion of water eliminated, and Curtius's anhydride belongs to the former class. In 1900 Fischer obtained

analogous products from the esters of  $\alpha$ -aminobutyric,  $\alpha$ -aminoisocaproic (leucine), and  $\alpha$ -amino-*n*-caproic acids, and classified them as diketopiperazines, in consequence of an observation by Mylius (1884), who prepared the anhydride of sarcosine. Realisation of the alternative type, glycylglycine, came in 1901, when, in conjunction with Fournau, Fischer hydrolysed diketopiperazine without detaching the two glycine molecules, and thereafter began that astonishing series of elaborations which culminated (1907) in the synthesis of an octadecapeptide,

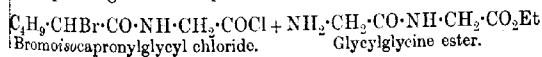
$\text{NH}_2\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_8\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot$   
 $[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_3\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_8\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
 composed of glycine (15) and *l*-leucine (3) molecules, and having the molecular weight 1213. The name "polypeptide" was adopted to emphasise the similarity to peptones displayed by the properties of the new class, whilst recalling the manner in which polysaccharides are compounded of simple carbohydrate molecules.

Subsequently to the process just reviewed, namely, arrested hydrolysis of a cyclic anhydride, two general methods were employed by Fischer to effect these imposing syntheses. Briefly stated, they depend on elongating the amino-acid chain at the basic and acidic terminals respectively. By the former mechanism a chloro- or bromo-acyl chloride, acting on the amino-acids (or polypeptides already synthesised therefrom), produces a halogen derivative, which only needs treatment with ammonia to become converted into the corresponding amino-compound, for instance, glycylalanine:



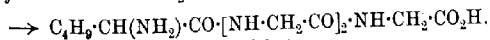
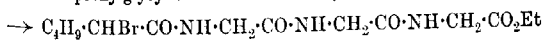
In this manner, the glycyl, alanyl,  $\alpha$ -aminobutyryl, leucyl, phenylglycyl, phenylalanyl, and prolyl ( $\alpha$ -pyrrolidinecarboxylic) groups were introduced (1903-1905).

The complementary process arose from the discovery (1904) that chlorides of halogenated acylamino-acids could be prepared by the action of phosphorus pentachloride on the acid dissolved in acetyl chloride; when such acyl chlorides act on the ester of an amino-acid or a polypeptide, the product only requires to be hydrolysed and treated with ammonia in order to yield the higher polypeptide corresponding to its component molecules:



Bromoisocapronylglycyl chloride.

Glycylglycine ester.



Leucyldiglycylglycine.



Although this process is elastic, there presented itself an experimental obstacle to great extension, namely, the solubility of many such acyl chlorides in acetyl chloride, and the consequent difficulty in separating them from solution without decomposition. This was overcome by preparing the acyl chlorides of the amino-acids or of the polypeptides themselves; these chlorides, having the general formula  $R\cdot CH(NH_3Cl)\cdot COCl$ , are also ammonium chlorides, and are generally not readily soluble in acetyl chloride. As they act smoothly on the esters of amino-acids and polypeptides, the device has been a most fruitful one, and particularly useful in application to the *D*- and *L*-amino-acids, with consequent synthesis of optically active polypeptides. Straightforward as these reactions appear in description, they represent a very remarkable feat experimentally, the rigid exclusion of water being necessary throughout.

Another advantage offered by this process is the facility with which it can be applied to elaborating polypeptides of diverse units, such as glycyl-*D*-alanylglycyl-*L*-tyrosine (1908), isomeric with the tetrapeptide which Fischer obtained in the previous year from silk hydrolysis, and herein lies the connecting link between these notable synthetic operations and the peptones arising from incomplete disruption of protein molecules.

The far-reaching consequence of the method provided by Fischer to separate the components of an amino-acid mixture has already been indicated, but the esters thus isolated were, until 1902, those of amino-acids only, unassociated with polypeptides. In that year, however, assisted by Bergell, he produced from silk fibroin, by successive hydrolysis with hydrochloric acid, trypsin and baryta, a dipeptide which appeared to be glycyl-*D*-alanine, although it could not be identified with the synthetic product; but in 1906, with Abderhalden, he obtained from the same source a methyldiketopiperazine,  $\begin{array}{c} NH-CH_2\cdot CO \\ | \quad | \\ CO\cdot CHMe\cdot NH \end{array}$  identical with that producible from

glycine and *D*-alanine, thus indicating that glycyl-*D*-alanine is amongst the degradation products of silk fibroin. Then followed the recognition of glycyl-*D*-tyrosine (silk fibroin), glycyl-*L*-leucine and *D*-alanyl-*L*-leucine (elastin), *L*-leucyl-*D*-glutamic acid (gliadin) and glycyl-*D*-alanylglycyl-*L*-tyrosine (silk fibroin).

It is obvious that the field of investigation opened by the foregoing experiments is limited only by material considerations, and an interesting calculation of the possibilities presenting themselves was made by Fischer in 1916. According to this, the octadecapeptide has 816 possible isomerides, whilst a polypeptide comprising 30 amino-acid molecules, of which 5 are glycine, 4 alanine,

3 leucine, 3 lysine, 2 tyrosine, 2 phenylalanine, and 13 various other descriptions, has a number of possible isomerides reaching  $1.28 \times 10^{27}$ . In these computations it is assumed that the mechanism of linking the amino-acid groups is limited to that of glycylglycine, but further complexity would arise from alternative junctions, such as that of diketopiperazine, the possibility of which was not excluded by Fischer. Moreover, he recognised that hydroxyamino-acids, such as tyrosine, serine, and hydroxyproline, may participate in the linkages peculiar to esters and ethers. Although the aggregate number of synthetic polypeptides must be well in excess of 200, this only serves to illuminate the gulf which still separates the chemical investigator from his goal. That Fischer appreciated this baffling factor to the fullest extent appears not only from his frequent references thereto, but also from the nature of his later synthetic operations. Following the octadecapeptide, these were directed more particularly to the association of optically active *Bausteine*, which were varied amongst themselves as much as possible with a view to synthesising those peptide fragments which possess the natural configuration, a property to be revealed by zymolysis. Drechsel's iodogorgonic acid from coral (1896), having been found identical with 2:5-iodotyrosine, was linked with glycine (1903), whilst *D*-valine,  $\alpha$ -aminostearic acid,  $\beta$ -aminobutyric acid,  $\alpha$ -methylisoserine, *L*-histidine, and *L*-proline were introduced also in the latter year, followed by *L*-cystine and *L*-phenylalanine; polypeptides containing *D*-tryptophan, isoserine, lysine, arginine, asparagine, *D*-glutamic acid and aspartic acid as components have since been prepared.

Although the simpler polypeptides are crystalline, and in that aspect bear no resemblance to the proteins, their tendency to amorphism increases with molecular weight, and aqueous solutions of the more complex ones are opalescent, yielding precipitates with ammonium sulphate, phosphotungstic acid, and tannin. Naturally, they do not respond to the colour test depending on tryptophan and tyrosine when those groups are absent, but they give the biuret reaction, and these features, in conjunction with their behaviour towards enzymes (see later), afford the strongest possible evidence in support of the protein diagnosis outlined by this chapter of Fischer's work. One passes to the next with the sensations of an explorer liberated from the perplexing entanglements of a dense forest to find himself on the shore of a limitless ocean.

*Zymo-chemistry.*

Since chemistry emerged from the crucible of alchemy, its association with biology has become increasingly intimate. Viewed materially, life is a process in which alternations of growth, decay, and regeneration present themselves in the light of chemical transformations, delicate, manifold, and inscrutable. Within the tissues of a living organism there proceed perpetual analyses and syntheses of which we gain an occasional glimpse, but cannot hope, by the comparative brutality of the test-tube, to stage the likeness. Nature's agents are photosynthesis and enzyme action, magic wands which transform carbon dioxide, water, and nitrogen into carbohydrates, fats, and proteins, and which, having synthesised these materials in plants, empower animals to analyse them and assimilate the products of disintegration. In the words used by Fischer during his Faraday Lecture, 1907, "the ultimate aim of bio-chemistry is to gain complete insight into the unending series of changes which attend plant and animal metabolism."

Having now reviewed some of his most important contributions to our knowledge of the building materials, and proceeding to consider the use which he made of the enzymes themselves, it is noteworthy that this began on a by-road of the great thoroughfare which he cut through the realm of carbohydrates. In 1889, having shown that the "seminose" produced by Reiss from vegetable ivory (*Phytelephas macrocarpa*) is identical with mannose, he isolated alcohol from the products of fermenting that sugar, and in the following year cultivated yeast in solutions of *dl*-mannose and  $\alpha$ -acrose (*dl*-fructose); in each case, the *d*-component was devoured, and thus *l*-mannose and *l*-fructose were isolated.

In 1894, assisted by Thierfelder, Fischer made a comparative study of natural and synthetical monosaccharides in respect of their attitude towards various families of yeast, from which it followed that whilst *d*-mannose, *d*-fructose, and, in lower degree, *d*-galactose resemble *d*-glucose, the yeasts are indifferent towards *d*-talose, *l*-mannose, *l*-glucose, sorbose, *l*-arabinose, rhamnose,  $\alpha$ -glucoheptose and  $\alpha$ -gluco-octose. This indicated that the fermentative principle of yeast is an asymmetric agent which is capable of attacking only those molecules of which the geometrical form does not differ too widely from that of *d*-glucose. It suggested also the possibility that, by persuasive tactics, a reluctant yeast might be tempted ultimately to modify its inherited taste and to accept as nutriment a sugar with which the asymmetry of its enzyme was not originally harmonious. This possibility has not yet been definitely realised.

Pasteur's notable discovery in connexion with *Penicillium* was

thus recalled, and, on extending the inquiry to natural and artificial glucosides, Fischer found that these materials arrange themselves into distinct groups in respect of their behaviour towards air-dried yeast extract (maltase) and emulsin, the  $\alpha$ -*d*-glucosides being hydrolysed by maltase and indifferent to emulsin; the latter, however, hydrolyses the  $\beta$ -*d*-glucosides, which are not attacked by maltase, both enzymes being without action on *l*-glucosides, *d*-galactosides, arabinosides, xylosides, rhamnosides, and glucoheptosides. Maltose is hydrolysed by the yeast extract, not by emulsin, whilst lactose displays the converse behaviour. It was by observations such as these that Fischer was led to emphasise the close relationship connecting the configuration of a sugar with that of the enzyme which attacks it, and to depict the mechanism of enzyme action by the simple analogy of a lock and key.

In the same year one of the many rocks which await the unwary voyager on this particular ocean was charted by Fischer. The "invertase" of that period was precipitated by alcohol and did not hydrolyse maltose, but Fischer replaced the solid material by an aqueous extract of air-dried (Frohberg) yeast; this does hydrolyse maltose, but neither the disaccharide nor  $\alpha$ -methylglucoside is affected by an aqueous extract of the fresh yeast which has not been dried, although cane-sugar is inverted. After being ground with powdered glass, the same yeast yields an extract capable of hydrolysing maltose and  $\alpha$ -methylglucoside, but the action is much more feeble than when the glucosides are left in contact with the suspended organism which has been narcotised. In consequence of divergent observations by G. H. Morris, it was found that complications are introduced by the proportion of chloroform employed, and this led to the use of toluene in its place.

The foregoing imbroglío emphasised the importance of specifying an enzyme by some reference to its origin, because an enzyme from one source is almost invariably associated with others, differing from those which accompany it when the origin is different. Fischer showed that whilst the extract of dried yeast hydrolyses both cane-sugar and maltose, the enzyme producing the latter effect cannot be invertase, because individual yeasts which contain invertase fail to hydrolyse maltose; moreover, invertase purified by alcohol is also indifferent towards this disaccharide. The specific maltoclastic enzyme had been called glucase by other workers, and it was for this name that Fischer substituted maltase, previously used by Bourquelot.

Lactose, which is indifferent towards brewer's yeast, is fermented by the milk-sugar yeasts, *S. Kefir* and *S. Tyrocola*. It had been claimed by Beyerinck, on somewhat slender evidence, that these

contain an enzyme, lactase, capable of hydrolysing lactose prior to fermentation; this was established by Fischer, who showed that the same result, intensified, was produced by kefir granules. Other observations of this period related to trehalose and melibiose, and it appeared to follow as a general conclusion that disaccharides are not fermented as such, but only in consequence of a preliminary hydrolysis by a specific enzyme.

In 1898 Croft Hill showed that the hydrolytic action of yeast maltase is reversible, a disaccharide being produced when that enzyme acts on glucose in concentrated solution; subsequently, Emmerling regenerated amygdalin by the action of yeast maltase on a mixture of mandelonitrile-glucoside and glucose, whilst Hanriot revealed the esterifying effect of lipase. In 1902 Fischer and E. F. Armstrong subjected a mixture of glucose and galactose to the action of kefir lactase, and, having removed the unchanged monosaccharides by fermentation, found in solution a disaccharide, which they called *isolactose*, observing that in its behaviour towards enzymes it stands midway between lactose and melibiose; moreover, the kefir lactase which links its generators has the power to separate them.

Impressed with the differences in chemical behaviour revealed by the enzymes of micro-organisms, Fischer turned attention to secretions of animal origin, and in 1896, assisted by Niebel, studied the attitude of starch, glycogen, maltose, lactose, sucrose, trehalose, amygdalin, and some artificial glucosides towards blood serum from several sources and a great variety of tissue extracts and juices. It was in the domain of proteins and polypeptides, however, that the principal use was made of these agents. In 1903, when his fruitful association with Abderhalden began, casein was subjected to protracted hydrolysis by the pancreatic enzyme, with the surprising result that proline and phenylalanine, although liberated from the protein by acid and alkaline hydrolysis, were not recognisable amongst the products. These were tyrosine, alanine, leucine, glutamic acid, aspartic acid, and a polypeptide material which, when hydrolysed by hydrochloric acid, gave an amount of the two missing amino-acids in close correspondence with the quantity obtainable from casein itself, together with alanine, leucine, glutamic acid, and aspartic acid. It was also found that edestin, haemoglobin, egg-albumin, fibrin, and serum-globulin resemble casein in the foregoing aspect, and thus was revealed a product of hydrolysis lying between the peptones and the amino-acids.

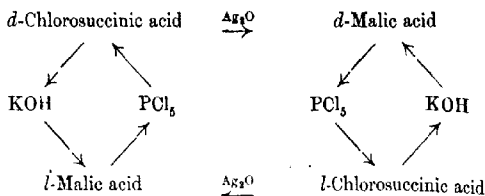
Acceptance of the relationship between proteins and amino-acids, established by the interposition of polypeptides, involves the

susceptibility of these materials to zymolysis, and, as their number grew, Fischer accumulated many studies of such action. Thus with Bergell (1903) he found that under conditions which favour the tryptolysis of naphthalenesulphoglycyl-*L*-tyrosine and carboethoxyglycyl-*DL*-leucine there is no change with glycylglycine, naphthalenesulphoglycyl-*D*-alanine, and hippuric acid; later it was shown that glycyl-*L*-tyrosine and leucylalanine may be tryptolysed, the disruption of the latter resembling that of carboethoxyglycyl-leucine by giving rise to active products. This branch of inquiry was greatly extended with the assistance of Abderhalden in 1905, when twenty-nine polypeptides were differentiated by their behaviour towards the tryptic enzyme, leading to conclusions based on the number, individuality, and configuration of the amino-acids involved. At the same time, it was found that glycyl-*L*-tyrosine, dialanylecystine, leucylalanine, leucylglycine, and leucylleucine are not hydrolysed by pepsin-hydrochloric acid.

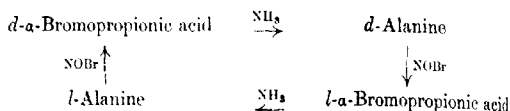
Thereafter, the development of this field has been left to other workers, of whom Abderhalden is recognised as the pioneer, and the remarkable achievements of the subsequent period are a splendid tribute to Fischer's foresight and genius in laying the foundations of a branch of science at once so complex and so fundamental. He it was, indeed, who first clothed with systematic experimental observations and established facts the dictum of Berzelius (1837) "that in living plants and animals there take place thousands of catalytic processes between tissues and fluids."

#### *The Walden Inversion.*

Prior to 1895, the conversion of an optically active substance into its enantiomorph had been accomplished only by racemisation preliminary to resolution by one of Pasteur's methods. The system of cyclic changes dating from that year, and classified as the "Walden inversion," exhibited a direct reversal of rotatory power, and offered, perhaps, the most elusive amongst the many interesting problems connected with optical activity. Walden showed that each chlorosuccinic acid will give both malic acids according to the agent selected for replacing halogen by hydroxyl; silver oxide leaves the sign unchanged, whilst potassium hydroxide produces an acid of opposite sign. As the regeneration of chlorosuccinic acid from malic acid by phosphorus pentachloride also involves a change of sign, the typical Walden inversion is represented as follows:

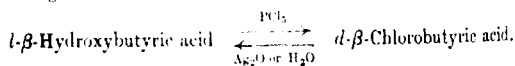


During the years 1907—1911, Fischer described numerous examples of sign-reversal arising from the study of amino-acids, for instance,

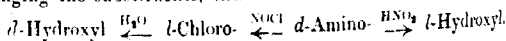


In the foregoing cycle it is a matter of indifference whether the replacement of halogen by an amino-group takes place in the acid or in the ester, but the converse change, attended by reversal of sign when alanine is transformed into  $\alpha$ -bromopropionic acid, proceeds without reversal when alanine ester is converted into  $\alpha$ -bromopropionic ester, the latter yielding, when hydrolysed, an acid having the same sign as the alanine employed. Other amino-acids, such as leucine, aspartic acid and phenylalanine, are distinguished from their esters in the same way, but *l*-valine ( $\alpha$ -amino-*isovaleric* acid), whilst giving with nitrosyl bromide *d*- $\alpha$ -bromo-*isovaleric* acid, is regenerated by the action of ammonia on that substance. Fischer found, also, that whilst *l*-lactic acid arises from *l*- $\alpha$ -bromopropionic acid by action of silver oxide, this agent converts *l*- $\alpha$ -bromopropionylglycine into a hydroxy-compound which gives *d*-lactic acid on hydrolysis. Furthermore, although *l*-valine is produced when ammonia acts on *d*- $\alpha$ -bromo-*isovaleric* acid, *d*-valine arises from hydrolysing the product of *d*- $\alpha$ -bromo-*isovaleryl*glycine and ammonia.

At first it was believed that this type of change is associated only with  $\alpha$ -substitution, Fischer and Scheibler showing that the following transformations are free from reversal of configuration:

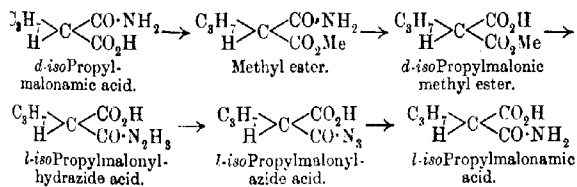


In 1911, however, they found that each  $\beta$ -aminobutyric acid will give both  $\beta$ -hydroxybutyric acids, according to the method of changing the substituents, thus:



The same year witnessed a comprehensive survey of the subject by Fischer (*Annalen*, 1911, **381**, 123), who described an ingenious model in which the central carbon atom and the movable groups have bristle-covered faces to facilitate their attachment in selected positions; thus the four substituents may be moved at the same time over the spherical surface of a central carbon atom, or they may be transferred singly to positions adjacent to those which they previously occupied. He represented substitution as preceded by the formation of an additive compound, which, on disruption, may or may not lead to a relative distribution of the substituents; thus the entrant group need not take the place of the one it dislodges, and if it assumes another position, the configuration of the product will differ from that of the original material. Viewed in this light, the Walden inversion is a normal process determined by the chemical agents employed and by the nature of the other groups attached to the asymmetric carbon atom. Simultaneously, the problem was discussed by Werner from the standpoint of supplemental valency, and criticisms by Biilmann in the following year led to a rejoinder by Fischer; it is not the purpose of this reference, however, to do more than indicate his contact with the subject, which still awaits a complete explanation.

Two important deductions from the theory of the asymmetric carbon atom received experimental confirmation at the hands of Emil Fischer by methods which the Walden inversion cannot vitiate, because the involved groups remain attached to the central nucleus throughout the changes. Assisted by F. Brauns, in 1914 he showed that optical activity disappears when two of the different groups become identical, producing ethylisopropylmalonic acid (inactive) from *d*-ethylisopropylmalonic acid. He next made the following transformations:



Since the original *d*-isopropylmalonic acid has  $[\alpha]_D$  48.8°, and the resulting *l*-acid  $[\alpha]_D$  -44.4°, agreement is sufficiently close to prove that the expectation of sign-reversal following systematic interchange of two substituents in an asymmetric system has been experimentally realised.



*Technology.*

Fischer's relationship to the chemical industry was intimate and beneficent. Viewed superficially, the subjects on which is founded his unrivalled reputation as an investigator do not appear to have much bearing on factory problems; but the value of a life-work cannot be estimated with accuracy unless the qualities of the worker are taken into account. It is a common observation that absorption in laboratory practice, coupled with unremitting study and theoretical reflection, tend to draw the chemical investigator so much away from practical affairs as to diminish his perception of commercial and industrial factors. Either because of his early training, or owing to his inborn love of knowledge in all its branches, Fischer was unusually free from this disability, and the reliance placed on his opinions by leaders of the German chemical industry ultimately grew into an attitude of trust which was quite exceptional. As early as 1883 he was a marked man, for in that year the chairman of the Badische factory selected him as director of research, in succession to Caro, at a salary of £5000, but the offer was not accepted. Whilst it is impossible to compute the results which might have accrued from his occupancy of the post, it is equally impossible to regret the decision which he then made. Although so tempting a proposal could not detach him from his chosen course, he remained throughout life in close communion with factory operations, becoming and continuing *persona grata* with the chemical industrial magnates and exerting a profound influence on the industry.

Probably his greatest direct contribution to technology lies in the stream of young chemists passing regularly from his laboratory to the factories, men soundly trained in the methods of systematic inquiry and in whom a love of chemistry had been made fruitful by the radiation of his galvanising personality. Nevertheless, more concrete associations with manufacture emerge from time to time. Phenylhydrazine was destined to become one of these, although its contact with industry through antipyrine, pyramidone, and tartrazine was made by other hands.

As already noticed, it might have been expected that the subject of his thesis for the doctorate, fluorescein, and the important contribution to the structure of triphenylmethane colouring matters for which he and his cousin were responsible so early in life, would have committed him definitively to the chemistry of dyes; but his interest in biochemistry rapidly became absorbingly predominant, and it was consequently in the field of synthetic drugs that his

personal connexion with chemical industry became most fruitful. Based on principles developed in his laboratory, methods were adopted in the Böhringer and Bayer factories for the manufacture of caffeine, theophylline, and theobromine, whilst the practicability of replacing atropine by a synthetical substitute may be traced to his early work on triacetonalcalamine.

A very definite contribution to manufacturing practice was made in 1903, when the improvement which he effected in the production of diethylbarbituric acid, arising from his work on purines, led to that substance becoming one of the most valuable hypnotics in pharmacy under the name veronal, the manufacture being undertaken by the Merck, Bayer, and Höchst factories. His collaborator in that work, von Mering, was associated with him also in 1907, when calcium iodobenenate, or sajodin, was brought out as a tasteless preparation of iodine easily tolerated by the organism. This was followed by calcium dibromobenenate, or sabromin, as an instrument for introducing bromine, and the production of both remedies was undertaken by the Bayer and Höchst factories, the latter developing also the preparation of strontium chloroarsinobenenate, or elarson, in connexion with which the preliminary experiments were made by Fischer and Klemperer. When war broke out he was taking part in the search for a carcinoma remedy, that path so thickly strewn with hopes deferred.

It is not difficult to imagine the demands which were made on his energy and wisdom during the five years which were destined to be the closing period of his life, and these have been delineated by A. von Weinberg. It is now known that the war could not have been continued by Germany beyond the middle of 1915 had not synthetic nitric acid begun to take the place of Chile saltpetre. The probable course of events revealed itself to Fischer in September, 1914, when he urged on the Westphalian manufacturers the need of prompt action, and was rebuked in consequence by the military authorities; but on October 1st he made a detailed report to the War Ministry with reference to the possibility of increasing the supply of ammonia from coke-ovens, and his services were in constant requisition during the growth of the synthetic nitric acid industry, which subsequently reached such enormous proportions.

Two months later the diminishing store of camphor led him to recommend the use of dimethyl- and diethyldiphenylcarbamide in powder stabilisation, these being actually adopted, and in February, 1915, he was presiding over a commission for stimulating the production of benzene and toluene by gas-stripping. Whilst the commission accomplished its original purpose before the end of that year, it remained in being to deal with such matters as the pro-

duction of heavy oil from naphthalene, the extraction of phenol and cresol from coke-oven tar, and, at the beginning of 1916, with a search for applications of the superabundance of benzene which then existed. By the end of that year, however, the Hindenburg programme had shattered the technical scheme for providing a sufficiency of this hydrocarbon, and converted plenty into famine; Fischer then demanded the demobilisation of 50,000 coal-miners.

As early as 1915 his attention was directed to the dwindling of pyrites reserves, and he became president of a gypsum and kieserite commission, charged with inquiry into means for utilising the sulphur content of those minerals; although technical difficulties prevented the application of kieserite to this purpose, the obstacles connected with gypsum were overcome and much valuable information was obtained.

At the beginning of 1916 Germany found it necessary to limit the saponification of fats, and Fischer was invited to examine more closely the alternative sources of glycerol. His first idea being to replace that substance by glycol, he recommended the construction of a factory at Essen for that purpose, but the subsequent process of Connstein and Lüddecke for producing glycerol by fermentation obviated the need for this measure. He took an active part in developing the new industry, in utilising the aldehyde-alcohol which offered itself as a by-product, and in solving the cognate problem of converting fatty acids to service as food, the result of which was ester-margarine.

It was the food shortage in all its aspects, however, which claimed his attention more and more pressingly. Interwoven with the demands of the explosives industry came the call for nitrogen fertilisers, and in January, 1917, associated with Nernst and Haber, he urged on the War Ministry the need for a foodstuffs commission to assume the task of stimulating food production on behalf of men and animals. With terrible earnestness he portrayed the secondary position occupied by patriotic heroism in relation to physiological law, the neglect of which must lead inevitably to psychological breakdown. From that time until its final session in 1918, the commission attacked with feverish energy a multitude of diverse problems, amongst which the conversion of straw into a digestible fodder for horses and cattle took a prominent place. The possibilities of wood, also, were explored from this point of view, the utilisation of leaves, rushes, and couchgrass (quitch), the germination of grain, and the preservation of vegetables. With special attention Fischer devoted himself to providing a coffee substitute, improving considerably on the knowledge which he had accumulated prior to the war, whilst attempts to augment the

supply of albuminoid esculents emerged in "mineral yeast" and the utilisation of lupines.

In spite of all these efforts, however, Fischer and his colleagues foresaw the inevitable results of increased disease, diminished capacity for work, and impaired moral resistance arising from the lamentable condition of the people. They embodied their conclusions in a memorial addressed to the heads of military and civil government in January, 1918, explaining the helplessness of science and technology to meet the situation, but their representations were unheeded.

### *Conclusion.*

Harassed by these distractions and anxieties, tormented from time to time by bodily pain, and bowed down by the loss of his second and third sons, his inextinguishable spirit found refuge in the calm pursuit of scientific inquiry. It was during this period that his life-long work on carbohydrates and the correlation of these with depsides received many decisive additions, and in the closing months of 1918 he witnessed, in the establishment of the "Deutsche Gesellschaft zur Förderung des Chemischen Unterrichts," the launch of an enterprise very near to his heart. As the war continued, he had become gravely concerned at the diversion of young chemists to its requirements, and the consequent injury to the scientific spirit of the new generation. To assist in combating this danger and the accompanying embarrassment to teaching institutions arising from the diminished value of money, he raised a considerable fund, which, in his own words, constituted "der letzte Dienst den ich der deutschen Wissenschaft leisten kann."

In this connexion, it should be remembered also that it was largely by the inspiration and energy of Emil Fischer that the idea of establishing a research foundation independent of teaching duties ultimately took shape in the Kaiser-Wilhelm-Institut für Chemie. Associated with Nernst and Ostwald, he had invited a company, amply representing both science and industry, to discuss preliminaries in October, 1905, but it was not until March, 1908, that the "Verein Chemische Reichsanstalt" was legally registered for the purpose of advancing chemical science and technology. Although a suitable site at Dablen was allocated by the Prussian Treasury, and many substantial donations had been made, it was not until the projected foundation of the Kaiser-Wilhelm-Gesellschaft in 1910, and the subsequent co-operation of this body with the Verein, that constructive steps could be taken. These culminated in the ceremony witnessed by the German Emperor on October

23rd, 1912, when Fischer, in the name of the Verein Chemische Reichsanstalt, as president of the executive committee, transferred the building to the president of the Kaiser-Wilhelm-Gesellschaft.

His life-work has now been reviewed, but only another generation can grasp its full significance. We shall not survive to witness the momentous consequences of its impulse, but we can perceive that Emil Fischer, in one branch of science the master, gave a new meaning to another branch, physiology, inasmuch as he placed biochemistry on an assured basis. The germ of this profound influence may be traced to a remote inquiry completely detached, as it would then have seemed in the mind of its author, from the trend of its ultimate development. The effect which was destined to be produced on physiological chemistry by the discovery of phenylhydrazine in 1875 offers but another example of the constant interplay between fact and thought. Although twelve years elapsed before that base enabled him to claim the synthesis of a natural sugar, progress thereafter was rapid and sweeping. The array of synthetical carbohydrates which had been assembled by the year 1894 provided him with the material necessary for the fundamental discovery that the specific action of an enzyme is intimately related to the configuration of the substrate. In the wealth of practical achievement which followed this discovery, the applications of its underlying principle constantly recur. The classification of the glucosides was a substantial consequence, but far more important was the utilisation of tissue extracts in the study of artificial polypeptides, showing that it is only those constructed of the amino acids supplied by nature which yield to the attack of peptoclastic enzymes. Thus it may be claimed for Fischer that he forged and perfected a new and delicate instrument with which the investigator may solve abstruse problems in biochemistry, for when once the technique is acquired, the use of enzymes in configuration diagnosis is unapproached by ordinary chemical processes in respect of precision and rapidity.

Reflecting on the essence of life in its chemical aspect, regarding the act of living as a complex alternation of digestion, assimilation, and oxidation, the mind begins to arrange in one beautiful fabric the coloured strands from which is woven Fischer's contribution to the knowledge of the centuries. He not only regularised the most fruitful of laboratory methods for studying life processes, but he assembled more richly, and in greater variety than any other chemist, the materials on which those processes depend. Carbohydrates, glucosides, depsides, purines, and polypeptides have, during the years of his activity, been brought to our delighted vision and ranged in perspective by his control of enzymes. As

interpreted by him, we recognise amino-acids as the basis of our being. All this knowledge will give definite form to countless inquiries dealing with digestion and assimilation, and by shaping the problems connected with such changes will assist in taking that first and most important step towards solving them. Indeed, it is not unjustifiable to hope that further advances along the lines now firmly laid by his life-work may bring biochemists of a future period to a clearer view of that elusive province in which hormones and advtants (miscalled vitamins) exercise their subtle influence on the alchemy of living bodies.

Even when due allowance has been made for the storehouse of accumulated facts on which the chemists of his era were empowered to draw and for the variety of technique which was at their command, it can scarcely be claimed that in wealth of revelation and manipulative skill Emil Fischer is eclipsed by any of his predecessors. It is difficult to imagine that he can be surpassed by any of his successors; but, whether this be so or not, his achievement will remain for all time a monument of industry, a masterpiece of symmetry and a gospel of inspiration. His contemporaries, who have watched the growth of a wonderful structure with admiration and pride, may leave to posterity, in happy confidence, the office of enshrining his work in the history of their beloved science:

“ For Time shall with his ready pencil stand,  
Retouch your figures with his ripening hand,  
To future ages shall your fame convey  
And give more beauties than he takes away.”

CXXXI.—*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part III. Resolution of Phenylmethylethylazonium, Phenylbenzylpropylazonium, and Phenylbenzylallylazonium Iodides into Optically Active Components.*

By BAWA KARTAR SINGH.

IN Parts I and II of this series of researches (T., 1913, 103, 604; 1914, 105, 1972) the author has described the resolution of two members of a new type of enantiomorphous compounds,



the asymmetry, and consequently the optical activity, of which is associated with the presence of an asymmetric nitrogen atom.

The present investigation, which is a continuation of this work, is concerned with the resolution of phenylmethylethylazonium iodide, the previously determined value of the molecular rotatory power of which was considered to be rather low (*loc. cit.*), in addition to that of two other members, namely, *phenylbenzylpropylazonium* and *phenylbenzylallylazonium iodides*.

Phenylmethylethylazonium iodide was resolved with the aid of silver *d*-α-bromocamphor-β-sulphonate. The *IBdA* salt, being less soluble, separated in a crystalline form and gave, for the *l*-basic ion,  $[M]_D - 23^\circ$ , the maximum rotation of  $-30^\circ$  having already been obtained from the hydrogen tartrate (*loc. cit.*). It is thus very probable that the former value of  $-30^\circ$  is the maximum molecular rotatory power of the *l*-basic ion.

Another point of interest is that *l*-phenylmethylethylazonium picrate has almost identical values of  $[M]_D$  in chloroform and methyl alcohol solutions (see p. 1206), and it thus stands in noteworthy contrast with phenylbenzylmethylazonium picrate, the value of  $[M]_D$  of which is three times as high in chloroform as in methyl alcohol (T., 1914, 105, 1984). This points to molecular association of the latter picrate in chloroform, but, so far, this view has not been corroborated by a determination of molecular weights in the two solvents.

Phenylbenzylpropylazonium iodide could only be obtained in one way, namely, by the action of benzyl iodide on phenylpropylhydrazine. In this reaction, a very small amount of a hydriodide was also formed as a by-product. The action of propyl iodide on

phenylbenzylhydrazine gave two hydriodides melting at 146—147° and 162—163° respectively, besides ammonium iodide. No azonium iodide was, however, formed in this reaction. The action of propyl iodide thus seems to be abnormal, and was further studied on two other hydrazines. In the case of phenylmethylhydrazine, the sole product of the action of this iodide was ammonium iodide, and in that of phenylpropylhydrazine at first no product was formed, but on keeping the mixture for some time a very minute quantity of ammonium iodide was isolated. It may be suggested that the secondary hydrazine is slowly reduced to an amine and ammonia, and the latter substance combines with hydriodic acid to form ammonium iodide. The hydriodic acid may be produced from the hydrolytic decomposition of propyl iodide, and it very probably acts also as the reducing agent.

Phenylbenzylallylazonium iodide was prepared from the action of benzyl iodide on phenylallylhydrazine. This reaction was quite normal.

*Resolution.*—Phenylbenzylpropylazonium iodide was resolved by the aid of silver *d*-camphor- $\beta$ -sulphonate and *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate. In the case of the camphorsulphonates, the *dBdA* salt, being less soluble in a mixture of methyl alcohol and ether, first separated out. It has  $[M]_D + 357.5^\circ$  in methyl alcohol and  $+300.5^\circ$  in aqueous solution. The *lBdA* salt was obtained by recrystallisation from water, in which it is less soluble than the other component, and has  $[M]_D - 153.2^\circ$  in methyl alcohol and  $-190.9^\circ$  in aqueous solution. Taking  $[M]_D$  for the *d*-camphorsulphonic acid ion as  $+53^\circ$ , the *dBdA* salt gives  $+247.5^\circ$  and the *lBdA* salt  $-243.9^\circ$  for the *d*- and *l*-basic ions in aqueous solution respectively.

On the other hand, if we assume that the salts *dBdA* and *lBdA* behave normally in respect of the additive character of the molecular rotatory power of the two ions in aqueous solution, the value of  $[M]_D$  for the *d*-camphorsulphonic acid ion is deduced to be  $+54.8^\circ$ , and that for the basic ion  $\pm 245.7^\circ$  (see p. 1210).

The agreement between the above figures is sufficiently close, and the value of  $[M]_D$  for the *d*-camphorsulphonic acid as above deduced further shows that the two salts *dBdA*, *lBdA* have been obtained in a pure condition.

It has already been pointed out in the case of the camphorsulphonates of phenylbenzylmethylazonium (T., 1914, 105, 1973) that three cases may occur when an externally compensated base is crystallised with an optically active acid: (1) the two salts *dBdA*, *lBdA* crystallise separately, so that each may be readily isolated; (2) a partly racemic compound, *dBIB*, *2dA*, may be



formed, in which case resolution is impossible; (3) each crystal which separates may contain both the salts *dBdA*, *lBdA* in varying proportions; in other words, the two salts form solid solutions, one in the other, and resolution is very slow and incomplete. In the case of the camphorsulphonates of phenylbenzylpropylazonium, behaviour of two kinds (types 1 and 3) is observed. After some of the *dBdA*, *lBdA* salts are separated in a pure condition, the residual salt, having  $[M]_D$  about  $+35^\circ$ , consists of 46 per cent. of the *dBdA* and 54 per cent. of the *lBdA* component. On further crystallisation from water, as well as from a mixture of methyl alcohol and ether, resolution proceeds extremely slowly, as is seen from the rotation constants. It is thus clear that the two salts have formed solid solutions, one in the other, when their composition corresponds with 46 per cent. of the *dBdA* and 54 per cent. of the *lBdA* component.

In the case of the bromocamphorsulphonates, the *lBdA* component, which melts at a higher temperature, first crystallises from a mixture of methyl alcohol and ether. The *dBdA* component, on recrystallisation, is obtained as an oil, which could not be solidified. The pure *lBdA* salt melts at  $178-179^\circ$ , and has  $[M]_D + 71.2^\circ$  in aqueous solution.

Phenylbenzylallylazonium iodide was resolved with the aid of silver *d*-camphor- $\beta$ -sulphonate. The *dBdA* component, being less soluble in methyl alcohol, first separated out. It melts at  $147-148^\circ$ , and has  $[M]_D + 190.3^\circ$  in aqueous solution,  $+265^\circ$  in chloroform solution,  $+285.7^\circ$  in methyl alcohol, and  $+319.2^\circ$  in ethyl alcohol.

#### EXPERIMENTAL.

*Phenylmethylethylazonium d- $\alpha$ -Bromocamphor- $\beta$ -sulphonate*,  
 $\text{PhMeEt}(\text{NH}_2)\text{N}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_{14}\text{OBr}$ .

Finely powdered azonium iodide (25 grams) was added in small quantities at a time to one molecular proportion of silver *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate (37.6 grams) dissolved in boiling methyl alcohol on the water-bath. The contents of the flask were kept shaken, and, after the addition of the whole of the azonium iodide, the heating was continued for half an hour to complete the reaction. The methyl alcohol was distilled off, and the residue, consisting of solid silver iodide and the syrupy bromocamphor-sulphonate, was extracted in the usual way with methyl alcohol. On evaporating the methyl alcohol, an oily residue remained, which did not crystallise even on keeping for six days. It was again dissolved in alcohol, and precipitated as an oil by the addition of ether. After some time fine, needle-shaped crystals began to

appear, and a portion of the oil slowly became crystalline; this amounted to 9.7 grams and melted at 152–153°. The remaining portion of the oil did not crystallise even on keeping under ether for six months (Found: C=49.05; H=6.74.  $C_{19}H_{29}O_4N_2Br$  requires C=49.46; H=6.29 per cent.).

The rotatory power\* of the salt was determined at 29° in aqueous solution:

Substance.	Time.	$\alpha_D$ .	$[M]_D$ .
Gram.	—		
0.1738	—	+1.11°	+293.0°
0.1738	After 25 hours.	1.13	298.3

The above camphorsulphonate (8.8 grams) was dissolved in the least possible quantity of methyl alcohol and precipitated by gradual addition of ether, with the following result:

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	$\alpha_D$ .	$[M]_D$ .
A.....	2.2	154–155°	0.2960	+1.86°	+288.3°
B.....	5.9	155	0.1792 (in 20 c.c.)	1.12	286.6

Fraction *B* was submitted to the same process, and the rotatory power of fractions *C* and *D* into which it was resolved was determined, with the following result:

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	$\alpha_D$ .	$[M]_D$ .
C.....	2.1	155–156°	0.2184	+1.41°	+296.2°
D.....	3.0	154–155	0.2454	1.54	287.8

The rotatory power in all the above cases was determined in water at 29–30°. The lowest value of  $[M]_D$  for the *B*/*a* salt is about +287°, and since  $[M]_D$  for silver *d*- $\alpha$ -bromocamphor- $\beta$ -sulphonate (Pope and Read, T., 1914, 105, 809) is +310°, the molecular rotatory power for the *l*-phenylmethylethylazonium ion is –23° (287–310).

*dl*-Phenylmethylethylazonium Picrate,  
 $PhMeEt(NH_2)N \cdot O \cdot C_6H_4N_3$ .

This salt was obtained from the racemic azonium iodide in the usual way as yellow prisms melting at 110–111°. It is very readily soluble in acetone, less so in methyl alcohol, ethyl alcohol, or chloroform, moderately so in water, and insoluble in ether (Found: N=18.63.  $C_{15}H_{17}O \cdot N_3$  requires N=18.47 per cent.).

\* The given weight of the substance was dissolved in 19.9 c.c. of solvent, and the rotatory power determination was made in a 2-dm. tube about thirty minutes after solution. This applies to all the observations recorded in this paper, unless the contrary is stated.

*1-Phenylmethylethylazonium Picrate.*

The active picrate was prepared by adding an alcoholic solution of the bromocamphorsulphonate of the *l*-base to an alcoholic solution of picric acid. On concentrating in the cold, water was added, when yellow prisms separated, which, after one or more recrystallisations from alcohol and ether, melted and decomposed at 114–115°. A mixture of the *dl*- and *l*-picrate\* melted at 107–108°. It is very readily soluble in acetone, less so in methyl alcohol, ethyl alcohol, or chloroform, moderately so in water, and insoluble in ether (Found: N=18.14.  $C_{15}H_{17}O_7N_5$  requires N=18.47 per cent.).

The rotatory-power determinations gave the following values:

Substance. Gram.	Time.	Tem- perature.	$a_D$ .	$[M]_D$ .
0.2748 (in 20 c.c. methyl alcohol)	$\frac{1}{2}$ hr.	27.5°	-0.16°	-22.06°
	5 hrs.	27.0	0.17	23.4
0.2977 (in chloroform).....	—	27.0	0.186	23.56
	2 $\frac{1}{2}$ hrs.	27.0	0.18	22.08
	7 $\frac{1}{2}$ ..	28.0	0.17	21.51
	32 ..	27.0	0.10	12.67

The rotatory power of the above picrate is practically identical in both the solvents. This is noteworthy, as phenylbenzylmethylethylazonium picrate has  $[M]_D$  three times as high in chloroform as in methyl alcohol (T., 1914, 105, 1984). This is probably due to association of the molecules of the latter picrate in chloroform.

*as-Phenyl- $\alpha$ -propylhydrazine, PhPr·N·NH<sub>2</sub>.*

This was prepared by dissolving sodium, first obtained in a fine granular condition, by melting it under xylene and vigorous shaking during cooling, in the calculated quantity of phenylhydrazine at 180°, under diminished pressure, and treating the resulting sodium phenylhydrazine with propyl bromide (Michaelis, *Ber.*, 1897, 30, 2815). The secondary hydrazine was purified by conversion into its hydrochloride (silky needles), which melts at 147°, and not at 135°, as stated by Michaelis (Found: Cl=16.69. Calc.: Cl=19.57 per cent.).

*Phenyl- $\alpha$ -propylhydrazine hydroferrocyanide,*  
 $(PhPr·N·NH_2)_2H_4Fe(CN)_6$ ,

is obtained as a white precipitate by the addition of a concentrated solution of potassium ferrocyanide to a concentrated solution of phenylpropylhydrazine hydrochloride acidified with hydrochloric acid. It is successively washed with a little water, alcohol, and ether, and dried in a vacuum desiccator. It is very readily soluble

in water, but less so in alcohol. On exposing it to the air for some time, it acquires a violet-blue colour (Found: Fe=10.67; N=26.65.  $(C_9H_{14}N_2)_2H_4Fe(CN)_6$  requires Fe=10.85; N=27.14 per cent.).

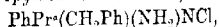
*dl-Phenylbenzylpropylazonium Iodide*,  $PhPr^+(CH_2Ph)(NH_2)NI$ .

(a) *By the Action of Benzyl Iodide on Phenylpropylhydrazine.*—An ice-cold ethereal solution of phenylpropylhydrazine (from 30 grams of the hydrochloride) was added to one molecular proportion of an ethereal solution of benzyl iodide, also cooled in ice. The crude product (33.5 grams), after recrystallisation from methyl alcohol and ether, melted and decomposed at 125—126°. In some experiments, the yield was even better. It is very readily soluble in methyl alcohol, somewhat less so in ethyl alcohol, still less so in water, and insoluble in benzene or ether (Found: I=34.61.  $C_{16}H_{21}N_2I$  requires I=34.49 per cent.).

From the filtrate, on keeping for some time, a very small amount of another substance separated. This was not an azonium iodide, but a hydriodide, as it gave an oil on treatment with a solution of sodium carbonate.

(b) *The Action of Propyl Iodide on Phenylbenzylhydrazine.*—The action of propyl iodide on phenylbenzylhydrazine did not give the azonium iodide obtained under (a), but what appeared to be a hydriodide, as the product gave an oil on treatment with sodium carbonate. The mother liquor, on keeping for several weeks, deposited a small amount of another substance which did not melt, but evolved ammonia with potassium hydroxide. It appeared to be ammonium iodide (Found: I=86.88. Calc.: I=87.6 per cent.).

*dl-Phenylbenzylpropylazonium chloride*,



is obtained in the usual way from the corresponding azonium iodide, and crystallises from alcohol and ether in colourless prisms melting and decomposing at 145—146°. It is very readily soluble in methyl alcohol, ethyl alcohol, acetone, or water, but insoluble in ether (Found: N=10.53.  $C_{16}H_{21}N_2Cl$  requires N=10.15 per cent.).

The corresponding *platinichloride* is a buff-coloured substance melting and decomposing at 151°. It is insoluble in water or organic media (Found: Pt=22.03.  $(C_{16}H_{21}N_2Cl)_2PtCl_4$  requires Pt=21.93 per cent.).

The *dl-aurichloride* is first obtained as an oil, which, on rubbing and allowing to remain, becomes crystalline. It recrystallises from

hot alcohol in yellow prisms melting and decomposing at 132–133°. It is very readily soluble in acetone, sparingly so in methyl alcohol, ethyl alcohol, or chloroform, and insoluble in water or ether (Found: Au = 34.08.  $C_{16}H_{21}N_2Cl \cdot AuCl_3$  requires Au = 34.0 per cent.).

On keeping for a few days in a stoppered bottle, it decomposes to a dark brown, semi-solid mass, hydrogen chloride being evolved.

*Phenylbenzylpropylazonium d-Camphor-β-sulphonate,*  
 $PhPr^+(CH_2Ph)(NH_2)N \cdot SO_3 \cdot C_{10}H_{16}O$ .

Finely powdered phenylbenzylpropylazonium iodide (30 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor-β-sulphonate contained in a mortar. Methyl alcohol, containing a few drops of water, was added to moisten the contents of the mortar, and the mixture was carefully triturated. This procedure was adopted in place of the usual one in order to diminish the decomposition which resulted when the constituents were heated together with ethyl acetate or alcohol. The mortar was kept in a vacuum desiccator, and the solid residue was extracted with methyl alcohol in a Soxhlet apparatus. On evaporating off the alcohol, 33.8 grams of the camphorsulphonate (theoretical yield, 38.4 grams) melting at 185° were obtained. It is very readily soluble in methyl alcohol, ethyl alcohol, acetone, or chloroform, moderately so in water, and insoluble in benzene or ether (Found: C = 65.88; H = 7.63.  $C_{27}H_{36}O_4N_2S$  requires C = 66.12; H = 7.63 per cent.).

*d-Phenylbenzylpropylazonium d-Camphor-β-sulphonate.*

The camphor-sulphonate (32.8 grams), as prepared above, was subjected to fractional precipitation by first dissolving it in the least possible quantity of methyl alcohol, and then gradually adding pure anhydrous ether. The following five fractions were obtained:

Fraction.	Yield, Grams.	M. p.	Substance, Gram.	$n_D^{20}$	$[\alpha]_D^{20}$
1	6.9	187°	0.1727	+0.76°	+206.7°
2	6.8	190–191	0.1858	0.145	36.65
3	16.7	189	0.1965	0.32	76.47
4	0.33	186	0.1982	0.307	72.75
5	1.7	184	0.1806	0.24	62.41

The rotatory power was determined in methyl alcohol at 30–31°. Fraction 1, after recrystallising several times, gave the pure *d*BdA salt melting at 190°, with the following values for rotatory power:

Solvent.	Tem- perature.	Time. Hours.	Substance. Gram.	$\alpha_D$ .	$[M]_D$ .
Methyl alcohol .....	24.0°	—	0.1340	+1.02°	+357.5°
Water .....	27.0	—	0.0963	0.616	300.5
" .....	25.5	23	0.0963	0.613	299.0
" .....	26.0	47	0.0963	0.61	297.5

Thus the pure salt, *dBdA*, melts at 190°, and has  $[M]_D$  +357.5° in methyl alcohol and +300.5° in aqueous solution.

*1-Phenylbenzylpropylazonium d-Camphor-β-sulphonate.*

Fractions 2 and 3 (amounting to 23.5 grams), after several further fractionations in the usual way, gave 6 grams of salt melting at 189°, which was optically inactive. The resolution in this way, however, proceeded very slowly, and as a preliminary experiment showed that the *lBdA* salt is less soluble in water, the optically inactive fraction was recrystallised from that solvent.

Fraction.	Yield. Grams.	M. p.	Substance. Gram.	$\alpha_D$ .	$[M]_D$ .
<i>a1</i> .....	2.0	188°	0.2280	-0.45°	-92.69°
<i>a2</i> .....	3.6	186	0.2073	+0.26	+58.92

Fraction *a1* was twice again recrystallised from hot water:

<i>a3</i> .....	0.55	190	0.1202	-0.485	-189.5
<i>a4</i> .....	0.2	189	0.1836	-0.64	-164.5

Fraction *a3* similarly gave fractions *a5* and *a6*:

<i>a5</i> .....	0.26	191	0.1459	-0.59	-190.9
After 20 hours:			0.1459	-0.58	-187.6
<i>a6</i> .....	0.18	—	0.1317	-0.51	-181.9
After 23 hours:				-0.47	-167.6

The rotatory power in the above cases was determined in water at 26—28°.

The rotatory power of fraction *a5* was also determined in methyl alcohol:

Substance. Gram.	Temperature.	Time. Hours.	$\alpha_D$ .	$[M]_D$ .
0.1159	25.5°	—	-0.373°	-151.1°
0.1159	26.0	24	-0.378	-153.2

Thus the pure salt, *lBdA*, melts at 191°, and has  $[M]_D$  -190.9° in aqueous solution and -151° in methyl alcohol (Found:  $N=5.81$ .  $C_{26}H_{36}O_4N_2S$  requires  $N=5.93$  per cent.).

After the pure salts, *dBdA* and *lBdA*, were isolated, there still remained about 15.6 grams of the substance with  $[M]_D$  ranging from +29° to +72°. It was repeatedly crystallised, first from ether and then from methyl alcohol and ether. Ultimately a salt with  $[M]_D$  +35° was obtained, when the rotatory power could

not be changed any further. It thus appears from the slow resolution that the two salts *d*BdA, *l*BdA have formed a solid solution one in the other. The rotation constants indicate that this fraction consists of about 46 per cent. of the *d*BdA and 54 per cent. of the *l*BdA salt.

*The Molecular Rotatory Powers of the Optically Active Ions in Aqueous Solution from that of the Camphorsulphonates.*

The molecular rotatory powers of the two camphorsulphonates, *d*AdB and *d*AlB, in less than 1 per cent. aqueous solution are tabulated below:

	M. p.	$[M]_D$ .
(1) <i>d</i> BdA .....	190°	+300.5°
(2) <i>l</i> BdA .....	191	-190.9

The algebraical sum of the molecular rotatory powers of these two salts in aqueous solution should be equal to twice the molecular rotatory power of the acid ion, and the algebraical difference should be equal to twice that of the basic ion. The value of  $[M]_D$  for the camphorsulphonic acid ion becomes 54.8°, and that for the phenylbenzylpropylazonium ion 245.7°. The agreement between the value of  $[M]_D$  for the camphorsulphonic acid ion as deduced above, and that obtained directly, as in the following table, is fairly close:

Temperature.	$[M]_D$ .	
20°	51.4° .....	(Graham, T., 1913, 103, 764).
20	51.6 } .....	(Thomas and Jones,
30	53.6 } .....	T., 1906, 89, 284).

*Phenylbenzylpropylazonium d-α-Bromocamphor-β-sulphonate,*  
 $\text{PhPr}^+(\text{CH}_2\text{Ph})(\text{NH}_2)\text{N}^+\cdot\text{SO}_3^-\cdot\text{C}_{10}\text{H}_{14}\text{OBr}.$

This salt was prepared by the gradual addition of finely powdered azonium iodide (36.1 grams) to one molecular proportion of silver *d-α*-bromocamphor-β-sulphonate dissolved in hot methyl alcohol. The heating was continued for half an hour on the water-bath under reflux. On filtering off the silver iodide and concentrating the methyl-alcoholic extract on the water-bath, an oil was obtained which at first did not crystallise. It was kept under ether overnight, when it solidified to colourless prisms (41.2 grams) melting at 144–148°. The compound is very readily soluble in methyl alcohol, less so in ethyl alcohol, acetone, or ethyl acetate, sparingly so in water, and insoluble in ether (Found: C=57.22; H=6.62; N=5.27.  $\text{C}_{26}\text{H}_{30}\text{O}_4\text{N}_2\text{BrS}$  requires C=56.63; H=6.35; N=5.08 per cent.).

*1-Phenylbenzylpropylazonium d- $\alpha$ -Bromocamphor- $\beta$ -sulphonate.*

The crude bromocamphorsulphonate (40.2 grams) melting at 144–148°, as obtained in the above way, was subjected to fractional crystallisation, as follows. It was dissolved in the least possible quantity of methyl alcohol and precipitated by gradual addition of ether. In several cases an oil separated, which increased the difficulty of resolution:

Fraction.	Yield. Grams.	M. p.	Substance. Grams.	$\alpha_D$ .	$[M]_D$ .
1	12.5	155–156°	0.1087	+0.54°	+272.0°
2	2.3	150–154	0.1193	0.68	312.2

Fraction 1 similarly gave:

3	3.2	178	0.1183	0.15	69.44
4	5.7	156–158	0.1362	0.742	298.4

Fraction 3, after several more recrystallisations, gave:

5	1.0	178–179	0.1792	0.22	67.31
		After 8 hours:		0.22	67.31
		After 23½ hours:		0.20	61.1

The rotatory-power determinations in the above cases were made in methyl alcohol at 30–32°. The rotatory power was also determined in aqueous solution in the case of fraction 5:

Substance. Gram.	$\alpha_D$ .	$[M]_D$ .
0.0693	+0.09°	+71.2°

Thus the pure *l*BdA salt melts at 178–179°, and has  $[M]_D + 71.2^\circ$  in aqueous solution and +67.3° in methyl alcohol (Found: N=5.13.  $C_{26}H_{35}O_4N_2BrS$  requires N=5.08 per cent.).

*dl-Phenylmethylpropylazonium Iodide, PhMePr<sup>c</sup>(NH<sub>2</sub>)NI.*

(a) *By the Action of Methyl Iodide on as-Phenylpropylhydrazine.*—Methyl iodide (6 grams) was added to one molecular proportion of *as*-phenylpropylhydrazine (6 grams) dissolved in ether. Within a short time, the mixture began to deposit a gummy mass, which, on keeping overnight, became crystalline. The crude substance (3.8 grams), after recrystallisation from alcohol and ether, separated in colourless prisms melting and decomposing at 106–107°. It is soluble in methyl alcohol, ethyl alcohol, or water, but insoluble in benzene or ether (Found: =43.26.  $C_{10}H_{17}N_2I$  requires I=43.48 per cent.).

(b) *Action of Propyl Iodide on as-Phenylmethylhydrazine.*—In



this reaction, the corresponding azonium iodide could not be obtained, but ammonium iodide was isolated (Found: I=87.87. Calc.: I=87.6 per cent.).

*Action of Propyl Iodide on as-Phenylpropylhydrazine.*—In this reaction, also, the corresponding azonium compound (namely, phenyldipropylazonium iodide) could not be obtained, but a small quantity of ammonium iodide was isolated.

*dl-Phenylethylallylazonium Iodide, PhEt(C<sub>3</sub>H<sub>5</sub>)(NH<sub>2</sub>)NI.*

Allyl iodide (5 grams) was added to one molecular proportion of *as*-phenylethylhydrazine dissolved in ether and cooled in ice. The mixture was kept overnight, when a gummy substance was deposited, which, however, solidified on rubbing. The crude product (2.4 grams), on recrystallisation from alcohol and ether, separated in colourless prisms melting and decomposing at 107–108°. The salt acquires a violet colour at about 100° (Found: I=42.09. C<sub>11</sub>H<sub>17</sub>N<sub>2</sub>I requires I=41.78 per cent.).

The corresponding *platinichloride* is obtained, in the usual way, as a pale orange precipitate, consisting of prismatic needles melting and decomposing at 151°. It is very sparingly soluble in cold methyl alcohol, but more readily so in hot, and insoluble in water, acetone, ethyl alcohol, benzene, or ether (Found: Pt=25.71. (C<sub>11</sub>H<sub>17</sub>N<sub>2</sub>Cl)<sub>2</sub>PtCl<sub>4</sub> requires Pt=25.62 per cent.).

*as-Phenylallylhydrazine, Ph(C<sub>3</sub>H<sub>5</sub>)N·NH<sub>2</sub>.*

This is prepared in the usual way by dissolving sodium in a finely divided, granular condition in phenylhydrazine, and treating the resulting sodium phenylhydrazine with allyl bromide (Michaelis and Claessen, *Ber.*, 1889, **22**, 2234). The secondary hydrazine is, however, best purified by leading hydrogen chloride into a chloroform solution of the base. *as*-Phenylallylhydrazine hydrochloride melts at 149–150°, and not at 137°, as stated by Michaelis and Claessen (*loc. cit.*) (Found: Cl=19.76. Calc.: Cl=19.22 per cent.).

*dl-Phenylbenzylallylazonium Iodide,  
Ph(CH<sub>2</sub>Ph)(C<sub>3</sub>H<sub>5</sub>)(NH<sub>2</sub>)NI.*

An ice-cold ethereal solution of *as*-phenylallylhydrazine (19.5 grams) was added to one molecular proportion of benzyl iodide (36.0 grams), also cooled in ice. Within a short time, colourless prisms began to deposit. The mixture was kept overnight, and

the crude substance (27.5 grams) melted and decomposed at 115—116°. On recrystallisation from hot alcohol, the temperature of decomposition was raised to 116—117°. The substance is very readily soluble in methyl alcohol, less so in ethyl alcohol, very sparingly so in water or benzene, and insoluble in ether (Found:  $\text{I}=34.89$ .  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{I}$  requires  $\text{I}=34.67$  per cent.).

*Phenylbenzylallylazonium d-Camphor-β-sulphonate,*  
 $\text{Ph}(\text{CH}_2\text{Ph})(\text{C}_3\text{H}_5)(\text{NH}_2)\text{N}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_{15}\text{O}.$

Finely powdered azonium iodide (23 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor-β-sulphonate contained in a mortar. The mixture was triturated thoroughly in the presence of a little methyl alcohol in the cold, in order to ensure complete double decomposition. It was repeatedly extracted with methyl alcohol, and, on evaporating the solvent by blowing air through the mixture, 18.1 grams of the camphorsulphonate (theoretical yield, 29.6 grams) were obtained. It is very readily soluble in methyl alcohol, ethyl alcohol, or acetone, less so in ethyl acetate or water, sparingly so in benzene, and insoluble in ether.

*d-Phenylbenzylallylazonium d-Camphor-β-sulphonate.*

The crude camphorsulphonate (24.3 grams), as obtained in the above way, was subjected to fractional crystallisation from methyl alcohol and ether. The pure salt, *dBdA*, melting at 147—148° and having a constant rotatory power, was obtained with great ease. As the rotatory power of this salt varies considerably with the nature of the solvent, the effect of this was studied on the action of constant rotatory power:

Solvent.	Time.	Substance. Gram.	$\alpha_D$ .	$[\text{M}]_D$ .
thyl alcohol .....	—	0.1143	$+0.78^\circ$	$+319.2^\circ$
"	After 54 hours.	—	0.74	302.8
"	" 22 "	—	0.72	294.6
"	" 51½ "	—	0.62	253.8
ethyl alcohol.....	" "	0.0645	0.394	285.7
"	" 21½ "	—	0.35	253.38
"	" 96 "	—	0.30	217.5
	(Solution slightly coloured.)			
chloroform .....	—	0.0971	0.55	265.0
"	After 23 hours	—	0.53	255.3
"	" 47 "	—	0.51	245.7
Water .....	—	0.0983	0.40	190.3

As the aqueous solution became turbid on keeping, no further readings could be taken. The mean temperature of all the above

observations was 27—29°. There is a marked mutarotation in the case of methyl alcohol and ethyl alcohol, but it is much less in the case of chloroform (Found: N=6.28.  $C_{26}H_{34}O_4N_2S$  requires N=5.96 per cent.).

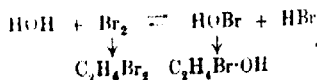
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[Received, July 20th, 1920.]

### CXXXII.—*The Preparation and Characterisation of Ethylenebromohydrin.*

By JOHN READ and REXFORD GEORGE HOOK.

ACCORDING to the somewhat scanty references available in the literature, it appears that ethylenebromohydrin has hitherto been prepared only in an impure condition. This remarkable fact in the case of so simple a substance is to be attributed not so much to instability as to the nature of the preparative methods adopted. Thus, in the older methods ethylene glycol was utilised as the starting point, the second reagent being either ethylene dibromide (Lourenço, *Ann. Chim. Phys.*, 1863, [iii], 67, 275), hydrogen bromide (Henry, *Jahresber.*, 1872, 304), or phosphorus tribromide (Demole, *Ber.*, 1876, 9, 48); whereas, more recently, application has been made of the interaction of ethyleneiodohydrin and bromine (Henry, *ibid.*, 1889, 1321), and the direct addition of hypobromous acid to ethylene (Mokiewski, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 900). Of the principles involved in these methods the last is undoubtedly to be preferred, as least liable to give rise to impurities in the resultant ethylenebromohydrin, and the advance which has lately been made in the experimental application of this principle (Read and Williams, *T.*, 1917, 111, 240; this vol., p. 359) has now enabled us to undertake the preparation of pure ethylenebromohydrin in quantity. At the same time, further study has been directed to the course of the reaction between ethylene and dilute bromine water, the investigation being facilitated by the observation that, as anticipated, the amount of bromohydrin formed during definite intervals may be estimated with sufficient accuracy by a titrimetric determination of the accompanying hydrogen bromide produced in accordance with the following scheme:



the results indicate a remarkable preponderance of bromohydrin in the initial stages of the reaction; thus, when the concentration of bromohydrin has reached 0.2*N* the molecular ratio of ethylenebromohydrin to ethylene dibromide is about 10:1, and in more dilute solutions the value is still higher.

The characteristics of the pure ethylenebromohydrin now obtained differ markedly from the data recorded by previous observers, the density at 20°, for instance, being 1.7629, as compared with the value 1.7195 at 18.6°, given by Henry (*loc. cit.*). In view of the specific interest of this substance as a simple derivative of ethyl alcohol and of its general potentialities as a synthetic agent, it seemed important to establish its main physical and chemical characteristics, and the present paper records some of the results of inquiries directed towards these ends.

#### EXPERIMENTAL.

##### *Preparation of Pure Ethylenebromohydrin.*

Bromine vapour and ethylene were passed into 1500 c.c. of distilled water under the conditions described previously (T., 1920, 7, 359), the operation being continued for several days, until 100 grams of bromine had reacted. The rate of absorption of the bromine, which was slow at first, increased appreciably as the reaction progressed. Ultimately the liquid was neutralised in the cold by the addition of solid sodium carbonate, and the aqueous layer was separated from ethylene dibromide. The latter, of which nearly half the total yield had volatilised in the course of the experiment, was shaken once with water in order to extract dissolved bromohydrin, and dried over calcium chloride; the yield amounted to 100 grams. The amount of hydrogen bromide produced in the reaction, estimated by titration with standard silver nitrate solution, corresponded with 35 per cent. of the bromine added, and thus indicated a 70 per cent. yield of ethylenebromohydrin. In order to prevent the eventual recovery of the bromine present as bromide, the aqueous solution was saturated at the ordinary temperature with anhydrous sodium sulphate rather than with sodium chloride or calcium chloride. Extraction of the bromohydrin was accomplished with three successive quantities of 250 c.c. of ether, and after drying over anhydrous sodium sulphate the ether was expelled in the water-bath.

Repeated distillation of the residual crude ethylenebromohydrin (100 grams) under atmospheric pressure demonstrated the impracticability of effecting an adequate purification by such a method.

The results were, however, of interest as throwing some light upon the varying boiling points, ranging from  $147^{\circ}$  to  $155^{\circ}$ , recorded for this substance by earlier investigators. On distillation, the temperature rose gradually to  $145^{\circ}$ , and the bulk of the liquid distilled between  $145^{\circ}$  and  $150^{\circ}$ , although distillation was incomplete even at  $155^{\circ}$ . The distillates were pale yellow and the residue dark brown, and an appreciable amount of hydrogen bromide was produced during the distillation. After several redistillations the purest material obtained in this way distilled between  $146^{\circ}$  and  $150^{\circ}$  ( $n_D^{20}$  1.4925;  $D_4^{25}$  1.7655, vacuum standard). On dilution with water to 60 per cent. strength a slight opalescence appeared, whilst at 50 per cent. a distinct second phase collected, and this persisted on further dilution. The second phase at 35 per cent. had  $n_D^{20}$  1.496, and was shown to contain ethylene dibromide. The purest ethylenebromohydrin obtainable by this method thus contains both ethylene dibromide and hydrogen bromide, as well as traces of water.

By conducting the distillation of the crude ethylenebromohydrin under diminished pressure, however, these impurities are readily eliminated. After the original removal of the ether, a little pure sodium carbonate is added, if necessary, to correct any acidity, and on distilling under diminished pressure a sharp delimitation occurs between the portion of low boiling point and the main fraction. In three different preparations the latter boiled smoothly and constantly at  $53.5^{\circ}/14$  mm.,  $54.5^{\circ}/14$  mm., and  $48.5^{\circ}/13$  mm. respectively, and no colour was developed during the distillation. The pure substance is neutral to litmus, and gives no opalescence when diluted with water or silver nitrate solution. As a rule, one distillation under diminished pressure yields a product conforming to these criteria, but sometimes a second distillation is necessary. The average primary yield of pure ethylenebromohydrin obtainable from 450 grams of bromine, in the manner outlined above, is about 120 grams, and further quantities may be extracted from the distillate of low boiling point and the original aqueous liquid. It may be mentioned that the extraction with ether from the aqueous solution is rendered more complete by previously saturating it with sodium sulphate at about  $30^{\circ}$  instead of at the ordinary temperature. Under such conditions a second phase, consisting mainly of ethylenebromohydrin, separates from the solution concerned, that is, from an approximately 1:2N-solution of ethylenebromohydrin containing also sodium bromide. This observation is in conformity with Comberg's experience with aqueous solutions of ethylenechlorohydrin (*J. Amer. Chem. Soc.*, 1919, **41**, 1426). The volume of ethylene required in practice for this preparation amounts, accord-

ing to our experience, to between twice and thrice the calculated quantity.

*Conditions affecting the Course of the Reaction between Ethylene and Dilute Bromine Water.*

The effect upon the course of the reaction utilised in the foregoing preparation of certain factors which may be subjected to variation has been discussed in former communications (*loc. cit.*); supplementary work of a quantitative nature has now been carried out in three directions in order to establish the influence upon this process of (1) concentration of the reaction-products, (2) temperature, and (3) light.

(1) For the purpose of ascertaining accurately the amounts of ethylenebromohydrin produced at various stages of the reaction, the determination, from time to time, of hydrogen bromide in an aliquot part of the reaction mixture proved to be satisfactory. In a control experiment, bromine vapour was passed into 500 c.c. of water under the usual conditions, the current of ethylene being replaced by one of air; after an interval of seven hours, during which a pale yellow tint had been maintained in the liquid, the volume of  $N/10$ -silver nitrate solution required by 5 c.c. was less than one drop, showing that no measurable decomposition of hypobromous acid into hydrogen bromide and oxygen had taken place under the conditions adopted.

In the succeeding preparations of ethylenebromohydrin the customary procedure was observed, except that the bromine was introduced in stages, the amount used being determined in each case by direct weighing. At the end of each stage the liquid was stirred for ten minutes after it had become colourless, and 5 c.c. of the liquid was then withdrawn and titrated with standard silver nitrate solution. Some of the results of two independent series of experiments are tabulated below. The calculations take into account the changes in volume which occur throughout the process, but it was considered unnecessary to apply a correction for the slight loss of bromine by diffusion. The original volumes of water used were 530 c.c. and 550 c.c. respectively, and in the second series a higher final concentration was attained than in the first series. The two sets of results are instructive as illustrating the order of the numerical discrepancies which may occur in determinations of this kind. It should be added that the temperature of the solution, which was ice-cooled, varied from about  $7^{\circ}$  to  $9^{\circ}$ , and that the experiments were conducted in diffused daylight.

Stage.	Total bromine present (grams).	Total bromine present as $C_2H_4Br\cdot OH$ +HBr (grams).	Percentage of total bromine reacting to form $C_2H_4Br\cdot OH$ +HBr.	Concentration of ethylenbromohydrin.	
				Grams per litre.	Normality.
<i>Series I.</i>					
1	4.26	4.05	95.1	5.9	0.048
2	12.95	11.85	91.5	17.5	0.140
5	52.56	44.02	83.8	65.0	0.520
8	100.66	76.73	76.2	112.4	0.899
12	160.44	111.00	69.2	161.8	1.294

<i>Series II.</i>					
1	4.00	3.77	94.3	5.3	0.043
2	12.10	11.09	91.7	15.8	0.126
4	51.36	43.26	84.2	61.7	0.494
7	97.67	75.06	76.9	106.6	0.853
10	167.90	111.29	70.5	156.9	1.255
15	230.41	148.31	64.4	207.6	1.661

These data show that the relative velocity of reaction between bromine and ethylene and hypobromous acid and ethylene respectively is displaced to the advantage of the former reaction as the products accumulate, a result which is probably connected with the great difference in solubility of ethylene dibromide and ethylenebromohydrin, and the separation of the dibromide as a distinct phase. Notwithstanding the change which has just been noted, the molecular ratio of bromohydrin to dibromide (which in the first stage was about 20:1) remained greater than unity throughout the range of concentrations investigated.

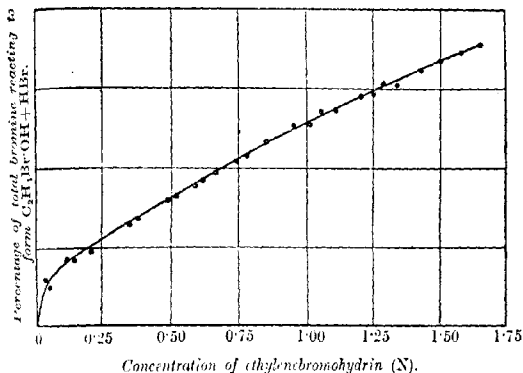
By plotting concentrations of ethylenebromohydrin in terms of normality factor ( $x$ ) against the corresponding percentages ( $y$ ) of bromine reacting to form ethylenebromohydrin and hydrogen bromide a regular curve is obtained (Fig. 1), the major portion of which is closely defined by two linear equations, namely, (i)  $y = 94.37 - 20.48x$ , and (ii)  $y = 89.99 - 15.47x$ . These equations embrace, respectively, the portions of the curve corresponding with (i)  $x = 0.125$  to 0.853, and (ii)  $x = 0.853$  to 1.661. The approximate yield of ethylenebromohydrin obtainable from a given amount of bromine, over this range of concentrations, is thus capable of ready calculation.

Attention was also directed to the rate of absorption of the bromine in these experiments; this was found, on the whole, to increase with the concentration of the solution, although irregularities were noticed. Twenty-one successive portions of 8 grams of

bromine took the following respective times, expressed in hours, for complete absorption when introduced with ethylene under the usual conditions into a volume of water originally measuring 530 c.c.: 1.9, 1.6, 1.6, 1.1, 1.1, 1.1, 1.2, 1.0, 0.9, 1.1, 1.1, 1.1, 1.3, 0.8, 0.8, 0.6, 0.5, 0.5, 0.5, 0.5, 0.5. The gradual acceleration in the rate of absorption may perhaps be attributed to an enhanced solvent action of the bromohydrin solutions on the ethylene, that is, to a progressive increase of the molecular concentration of this reagent. In other series of experiments the corresponding times were noticeably different, and it seems possible that the acceleration or retardation was due to the presence of small amounts of foreign substances.

(2) In order to test the influence of temperature on the reaction

FIG. 1.



it was conducted at  $35^\circ$ , after a preliminary control experiment had been carried out at the same temperature according to the principle indicated above. A constant volume of 250 c.c. was maintained throughout the experiment, water being added to replace the loss by evaporation. The volume of  $N/10$ -silver nitrate solution required by 5 c.c. of the liquid after the control experiment had been continued for four hours was 0.08 c.c. Thus, at  $35^\circ$  there appears to be a very slow decomposition of hypobromous acid into hydrogen bromide and oxygen, and a corresponding correction was introduced. It was also found necessary, when working at this temperature, to apply a correction for the loss of bromine by diffusion, which amounted to 1.20 grams in the control experiment.

On passing bromine vapour and ethylene into 250 c.c. of water



under the conditions of the control experiment, the amount of bromine utilised in the preparation of a 0.437*N*-solution of ethylenebromohydrin was 28.2 grams, after correcting for the loss by diffusion. Of this amount, 62 per cent. reacted to form ethylenebromohydrin and hydrogen bromide, as compared with 85.4 per cent. reacting in this way, for the same concentration, in the ice-cooled solution. The time taken was 14.5 hours, the corresponding time at the lower temperature being 10.0 hours. It is therefore apparent that by raising the temperature the reaction takes place more slowly, and that at the same time the molecular ratio of ethylenebromohydrin to ethylene dibromide is materially lessened.

The effects just noticed were accentuated at still higher temperatures, but owing to the considerable loss of bromine by diffusion at temperatures much above 35° quantitative examination was rendered difficult in such cases. From further experiments, to be described below, the second effect is somewhat more pronounced than indicated by the above figures, which take no account of the slow hydrolysis of ethylenebromohydrin occurring in warm aqueous solutions. The slower rate of reaction between ethylene and bromine water in warm solutions is probably to be attributed to the diminishing solubility of ethylene in water as the temperature rises.

(3) In the addition of hypochlorous and hypobromous acids to unsaturated substances it has usually been assumed that the reaction is favoured by conducting the operation not only at a low temperature but also in diffused light, or, preferably, in the dark. It was therefore of interest to investigate the influence of light upon the additive reaction between hypobromous acid and ethylene. In the short series of experiments summarised below, the ice-cooled water (530 c.c.) was exposed to direct sunlight during the passage of the bromine vapour and ethylene, and the progress of the reaction was followed in the manner already described. The result of a control experiment indicated that no appreciable decomposition of hypobromous acid took place under the conditions laid down.

Stage.	Total bromine present (grams).	Total bromine present as $C_2H_4BrOH$ + $HBr$ (grams).	Concen- tration of ethylene- bromohydrin ( <i>N</i> ).	Percentage of total bromine reacting to form $C_2H_4BrOH + HBr$ .	
				In sunlight.	In diffused light.
1	4.12	3.81	0.045	92.5	93.5
2	12.38	10.97	0.130	88.6	91.7
3	20.35	17.80	0.212	87.5	90.0
4	36.59	30.75	0.368	84.0	86.8

From the last two columns of the table it is seen that the values obtained in this series of experiments for the molecular ratio of

ethylenebromohydrin to ethylene dibromide are slightly lower than the values corresponding with the original conditions; the differences, however, are not marked. The time taken for the absorption was 2.75 hours, which is appreciably less than any corresponding period observed for an experiment conducted in diffused light. On the whole, therefore, the rather remarkable conclusion is reached that sunlight exerts an advantageous rather than a detrimental influence upon the additive reaction between hypobromous acid and ethylene.

*Physical Properties of Pure Ethylenebromohydrin.*

Ethylenebromohydrin is a colourless, mobile liquid, miscible with water in all proportions. Demole's statement (*loc. cit.*) that it is only sparingly soluble in water indicates contamination with ethylene dibromide. The solubility in water decreases considerably in the presence of certain salts, such as, for example, sodium chloride, calcium chloride, and sodium sulphate. The aqueous solutions possess a sweet, burning taste. The vapour of the pure substance or of its aqueous solutions, down to about 5 per cent. strength, produces a painful irritation of the eyes and nostrils shortly after inhalation. Ethylenebromohydrin dissolves readily in most of the common organic solvents, but forms a distinct phase when added to light petroleum. It distils unchanged under diminished pressure at the temperatures noted above; when the pure substance is heated under atmospheric pressure, however, it darkens as the temperature approaches the boiling point, and decomposition occurs with the production of hydrogen bromide. Distillation commences at about 150°, but the temperature fluctuates and the boiling point is indefinite.

The refractive index of several specimens was determined with the Abbé refractometer at 20° for the *D* line; the results were practically identical, the mean value being 1.4915. When the liquid was exposed for a few seconds on the prism this value sank in a typical instance to 1.479; this observation illustrates the pronounced hygroscopicity of ethylene bromohydrin. The observed molecular refractive power at 20° was 34.84, which stands in close agreement with the calculated value, 34.76.

Determinations of specific gravity (reduced to a vacuum) were as follows:

$$D_4^{20} 1.7902, D_4^{20} 1.7696, D_4^{20} 1.7629, D_4^{20} 1.7560, D_4^{20} 1.7494.$$

The mean coefficient of dilatation between 0° and 30°, calculated from the data obtained in the above determinations, is 0.00078.

\*  
*The Relationship between the Refractive Index and the Concentration of Aqueous Solutions of Ethylenebromohydrin.*

It has been shown by Irvine that measurements of refractive index provide a rapid and convenient method for the determination of the approximate strengths of aqueous solutions of ethylenechlorohydrin; the method has also been adopted, with useful results, by Gomberg (*loc. cit.*, p. 1418). For this reason, and also in view of certain interesting thermal changes and related phenomena which occur during the dilution of ethylenebromohydrin with water, it was considered advisable to undertake a refractometric examination of a series of aqueous solutions of this substance. Solutions of different concentrations were made by direct weighing of the constituents, and in each case the refractive index was determined with the Abbé instrument at 20° for the *D* line. Some of the observations are tabulated herewith:

Percentage by weight of ethylenebromohydrin.		Percentage by weight of ethylenebromohydrin.	
	$n_D^{20}$		$n_D^{20}$
100.000	1.4915	49.179	1.3915
95.340	1.4801	40.372	1.3790
90.032	1.4671	30.999	1.3667
80.007	1.4454	22.441	1.3561
72.201	1.4299	18.810	1.3517
60.586	1.4095	10.010	1.3422
53.620	1.3980	3.361	1.3358
		0 (water)	1.3330

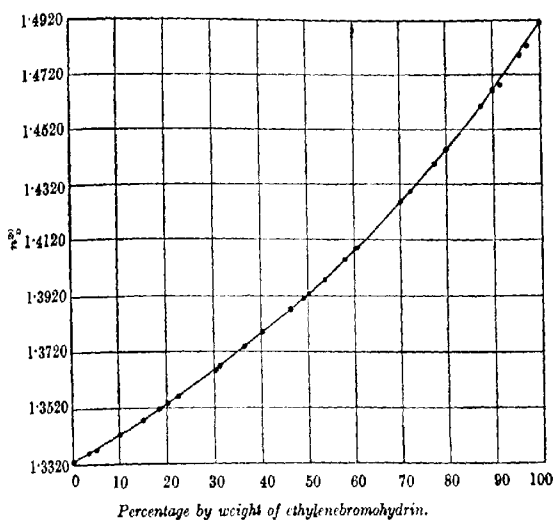
When the whole of the data are represented graphically, the resulting points lie on a regular curve which does not approximate to a straight line (Fig. 2). The character of the curve indicates that the refractive index of aqueous solutions of ethylenebromohydrin is always less than the value calculated from the admixture formula, that is, on mixing ethylenebromohydrin with water there is a contraction in volume. It is also to be observed that the value of the refractive index does not pass through a maximum, as in the case of ethyl alcohol (Doroshewski and Dvorschantschik, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 908). It is evident that the above curve furnishes a ready means of determining, with close accuracy, the concentrations of aqueous solutions of ethylenebromohydrin.

*The Distillation of Aqueous Solutions of Ethylenebromohydrin.*

From the general characteristics of ethylenebromohydrin it seemed probable that its dilute aqueous solutions, such as are obtained in the method of preparation outlined above, might be

concentrated by fractional distillation. In order to test this point, solutions of known strength were submitted to this operation, the various fractions being examined refractometrically. In the case of a 5 per cent. solution a first fraction, containing 3 per cent. of the total bromohydrin, had a concentration of 12 per cent. The concentrations of succeeding fractions were lower; when 20 per cent. of the total bromohydrin had been collected, the concentration of the next few drops of distillate was 9.5 per cent., and after the collection of 50 per cent. the corresponding value was 7.0 per cent.

FIG. 2.



The boiling point was originally  $100.0^\circ/766$  mm., and it rose eventually to  $100.1^\circ$ . The boiling point of water at the same pressure is  $100.22^\circ$ .

With a 30 per cent. solution a first fraction, containing 11 per cent. of the total bromohydrin, had a concentration of 34.0 per cent., and when two-thirds of the total bromohydrin had passed over the concentration of the next few drops of distillate was identical with that of the original solution, that is, 30 per cent. Meanwhile, the boiling point had risen from  $99.0^\circ$  to  $99.4^\circ$ ; the barometric height was 768.5 mm., corresponding with a boiling point of  $100.31^\circ$  for water.

These observations suggested that ethylenebromohydrin forms a mixture of constant boiling point with water at a concentration in the vicinity of 34 per cent. A similar distillation of a 34 per cent. solution confirmed this conclusion, the actual concentration of the constant-boiling mixture being 35.0 per cent., as is evident from the following table:

Fraction.	Boiling point.	Weight of fraction (grams).	$n_D^{20}$ .	Concentration per cent. of bromohydrin in fraction.	Percentage of total bromohydrin in fraction.
1	99.1	0.90	1.3718	35.1	3.0
2	99.1	2.06	1.3720	35.2	6.9
3	99.1	2.96	1.3717	35.0	9.8
4	99.1	3.22	1.3717	35.0	10.7
5	99.2	3.38	1.3716	34.9	11.2
6	99.2	3.44	1.3714	34.8	11.3
7	99.2	4.24	1.3708	34.3	13.7
8	99.5	4.35	1.3700	33.7	13.9
residue	—	6.11	1.3700	33.7	19.5

The constant boiling point of a 35.0 per cent. aqueous solution of ethylenebromohydrin is therefore 99.1°/762.4 mm., the corresponding boiling point of water being 100.06°. The residue from the above distillation possessed a faint yellow colour, and was distinctly acid; titration with standard silver nitrate solution showed that it contained 0.1491 gram of hydrogen bromide, evidently produced by partial hydrolysis of the bromohydrin during the distillation. The distillates contained a mere trace of the acid, and thus the percentage amount of the total bromohydrin hydrolysed in the course of the operation was 2.2.

Very interesting results were obtained by distilling more concentrated solutions of the bromohydrin, and a typical series of data is accordingly summarised below for the case of a 74.9 per cent. solution. The barometric height was 755 mm., corresponding with a boiling point of 99.82° for water.

Fraction.	Boiling point.	Weight of fraction (grams).	$n_D^{20}$ .	Concentration per cent. of bromohydrin.	Percentage of total bromohydrin in fraction.
1	99.5°	1.08	1.3708	41.0	2.0
2	100.0—101.0	3.03	1.3838	43.9	6.1
3	101.0—102.8	3.70	1.3880	47.0	8.0
4	102.8—109.1	3.84	1.3982	53.9	9.5
5	109.1—137.0	3.81	1.4332	74.0	12.9
6	137.0—147.4	4.51	1.4840	97.0	20.0
7	147.4—149.0	5.26	1.4912	99.9	24.0
residue	—	3.83	1.4905	99.7	17.5

When concentrated aqueous solutions of ethylenebromohydrin are distilled the water thus passes over in the initial stages of the operation, and eventually almost pure bromohydrin distils. In the

experiment described it was ascertained by titration that 0.9 per cent. of the total bromohydrin present was hydrolysed during the distillation. Of the hydrogen bromide formed it is interesting to note that 5 per cent. remained in the distilling flask, and 5 per cent. was present in fraction 5; the bulk was found in fractions 6 (60 per cent.) and 7 (30 per cent.). As fractions 6 and 7 thus contained 1.7 and 0.7 per cent. of hydrogen bromide respectively, the purity was distinctly lower than indicated by the refractive index. From these investigations it is seen that dilute aqueous solutions of ethylenebromohydrin might be concentrated by fractional distillation, but that in dealing with large quantities of such solutions the loss by hydrolysis would be considerable. This objectionable feature could be partly eliminated by conducting the distillation under diminished pressure.

#### *The Hydrolysis of Ethylenebromohydrin.*

The slight decomposition noticed during the distillation of aqueous solutions of ethylenebromohydrin seemed to indicate a greater susceptibility of this substance towards hydrolysing agents than is exhibited by ethylenechlorohydrin, and accordingly further observations were made in order to settle this point.

In the first place, when aqueous solutions of ethylenebromohydrin of concentrations ranging from 95 per cent. to 3 per cent. were prepared and examined at regular intervals no decomposition could be established until several weeks had elapsed. As a typical example, a 50 per cent. solution after remaining for a month at the ordinary temperature had developed a perceptible content of hydrogen bromide, corresponding with the hydrolysis of about 0.3 per cent. of the bromohydrin originally present; in the same period the refractive index had declined by 0.0007. With a 3 per cent. solution the amount hydrolysed in the same time approached 1 per cent. of the bromohydrin, and in general this very slow hydrolysis was most apparent in dilute solutions. At higher temperatures the velocity of hydrolysis in aqueous solution was much accelerated; on boiling a 6.25 per cent. solution for thirty minutes under reflux, 19 per cent. of the bromohydrin was hydrolysed, and in ninety minutes 44 per cent. was hydrolysed.

Silver nitrate produced no immediate reaction with cold aqueous solutions of the bromohydrin, but in dilute solutions an opalescence developed after fifteen or twenty minutes, and quantitative estimations made after longer intervals showed that the hydrolysis had undergone appreciable acceleration.

Seeing that ethylenebromohydrin is prepared in acid solution, it was of interest to ascertain the effect of acid on the rate of hydro-

lysis. A 1.8*N*-solution of hydrochloric acid containing 9.0 per cent. of ethylenebromohydrin was examined twenty-four hours after being prepared, but no perceptible hydrolysis had occurred in the cold. By boiling this solution for thirty minutes, 51 per cent. of the bromohydrin was hydrolysed, the presence of acid having therefore accelerated the reaction.

It was to be anticipated that alkali would exert a much more pronounced acceleration than acid, and, in fact, a 4.5 per cent. solution of ethylenebromohydrin, containing about two equivalent proportions of potassium hydroxide, was hydrolysed to the extent of 47 per cent. when allowed to remain at the ordinary temperature for thirty minutes. By boiling a similar solution for thirty minutes, 97 per cent. of the bromohydrin was hydrolysed, and ninety minutes' boiling brought about complete hydrolysis.

Lastly, an analysis of a pure specimen of ethylenebromohydrin by alkaline hydrolysis may be quoted: 0.2935 gram, after boiling for ninety minutes with an excess of sodium hydroxide solution, required 23.5 c.c. of *N*/10-AgNO<sub>3</sub>. Br=64.0. Calc., Br=64.0 per cent.

*Summary.*

1. Pure ethylenebromohydrin has been prepared in quantity by the action of cold dilute bromine water on ethylene, this method having been found preferable to any other which has been described for the purpose.

2. In the above reaction the molecular ratio of ethylenebromohydrin to ethylene dibromide decreases continuously with increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution, and also with rise of temperature, but it is not influenced markedly by sunlight. The reaction is hastened by cooling or by exposure to sunlight.

3. The main physical characteristics of ethylenebromohydrin, and also the relationship between the concentration and refractive index of its aqueous solutions, have been established.

4. Ethylenebromohydrin and water form a mixture of constant boiling point (99.1°/762.4 mm.) at a concentration of 35.0 per cent.

5. Ethylenebromohydrin is hydrolysed more readily than ethylenechlorohydrin. In cold aqueous solutions the hydrolysis is perceptible, although extremely slow; it is greatly accelerated by heat, also by the presence of acid, and, notably, of alkali.

Cognate investigations are in progress.

DEPARTMENT OF ORGANIC CHEMISTRY,  
UNIVERSITY OF SYDNEY.

[Received, August 30th, 1920.]

CCCCIII.—*The Propagation of Flame in Mixtures of Methane and Air. Part II. Vertical Propagation. Part III. Propagation in Currents of the Mixtures.*

By WALTER MASON and RICHARD VERNON WHEELER.

PART II.—VERTICAL PROPAGATION.

THE object of the experiments herein described on the vertical propagation of flame in mixtures of methane and air was to obtain information as to the magnitude of the effect of convection currents on the speed of the flame.

Except, perhaps, during the "uniform movement,"\* the transference of heat by convection currents clearly plays an important part in the transmission of flame, and is accountable for many of its phenomena. For example, the well-known fact that the limits of inflammability of gaseous mixtures vary with the position of the point of ignition according as the flame has to pass upwards or downwards through the mixture, more combustible gas being required to form a lower-limit mixture under the latter conditions, is explicable on the assumption that during the downward propagation of flame convection currents do not materially affect the transference of heat to unburnt layers of the mixture. A like explanation can be given for the fact that when mixtures of methane and air containing less than 7.5 and more than 12.5 per cent. of methane are ignited at the centre of a closed spherical vessel, flame reaches the bottom of the vessel later than it reaches the top by an interval of time which varies with the methane-content of the mixture (T., 1918, 113, 845).

In general, it would seem probable that flame should travel vertically in a given mixture more rapidly when it is ignited from below than when it is ignited from above, if only by virtue of the current produced by the heated gases. Under the special conditions of ignition at the centre of a closed vessel, however, any difference there may be between the speeds of upward and downward propagation of flame is inappreciable with mixtures in which

\* The "uniform movement" is the term generally applied to the initial slow propagation of flame at a uniform speed that occurs when an inflammable mixture is ignited at the open end of a horizontal tube closed at the other end. Under such conditions the propagation of flame is assumed by Le Chatelier to be "normal" and to be effected mainly by the conduction of heat from the burning to the unburnt gases.



the speed of flame is comparatively rapid (mixtures containing between 7.5 and 12.5 per cent. of methane). As bearing on this point, certain observations by Schloesing and de Mondésir on the combustion of mixtures of carbon monoxide and air should be noted. Having remarked that one rarely observes the "normal" propagation of flame because of the development of movements in the gaseous mixtures due to the combustion itself, they suggest that one of the principal causes of movement or agitation of the burning mixture is the difference in density between the heated and the cold gases: "Un mélange gazeux allumé par la partie inférieure, brûle toujours plus vite que lorsqu'il est allumé par la partie supérieure. Les gaz chauds s'élèvent en effet à travers les gaz froids avec une vitesse qui vient s'ajouter à la vitesse normale de propagation. Mais l'accélération ainsi produite est toujours très faible; elle n'est sensible qu'avec les mélanges gazeux très lents et renfermés dans des tubes de grand diamètre" (*Ann. des Mines*, 1883, [viii], 4, 298).

As regards the "uniform movement" (that is to say, "normal" propagation of flame), we drew the conclusion (T., 1917, 111, 1053) that if Le Chatelier's definition of it as "le mode de propagation par conductibilité" be accepted, it is a strictly limited phenomenon obtainable only in tubes within a certain range of diameter, large enough to prevent appreciable cooling by the walls, but narrow enough to suppress the influence of convection currents, so that the diameter of the tube in which the flames travel should be specified when speeds purporting to be those of the "uniform movement" or "normal" propagation of flame are recorded. Alternatively, the initial slow movement of flame at a uniform speed should be regarded simply as a particular phase in the propagation of flame that occurs when ignition is effected (in a quiescent mixture) at the open end of a straight, horizontal tube (of any diameter) closed at the other end, and not as resulting from a particular mode of heat transference.\* As a result of the present investigation, it is shown that the latter is the preferable, if not the only correct, way of regarding the uniform movement; for the idea that this "normal" propagation of flame is solely by conduction of heat from layer to layer of the mixture is untenable. Further, it is shown that there is a uniform régime in the propagation of flame from the open to the closed end of a straight tube

\* The influence of convection currents is noticeable with the fastest flames in mixtures of methane and air in tubes 10 cm. in diameter, the visible effect being a turbulence of the flame-front; whilst in tubes of smaller diameter (5 to 9 cm.), although there is no turbulent appearance, the shape of the flame-front shows that there is a definite movement of the hotter gases towards the upper part of the tube (T., 1914, 105, 2609).

when the tube is vertical and the direction of travel of the flame is either upwards or downwards.

*I. Ignition at the Open End of a Vertical Tube Closed at the other End.*—Under these conditions, the first phase in the propagation of flame in a horizontal tube is the uniform movement. If this uniform movement of flame in a horizontal tube represents essentially the transference of heat by conduction from layer to layer of the mixture, similar conditions of ignition with a vertical tube should produce a similar uniform movement when the open end of the tube is above, so that the flame travels downwards; for convection currents cannot then be held to play a greater part in the transference of heat to the unburnt mixture than when the flame is travelling horizontally. Moreover, the initial speeds of the flames in like mixtures during their downward propagation in a vertical tube and during the uniform movement in a horizontal tube should be approximately the same, at all events in narrow tubes in which the action of convection currents during horizontal propagation may be assumed to be at a minimum.

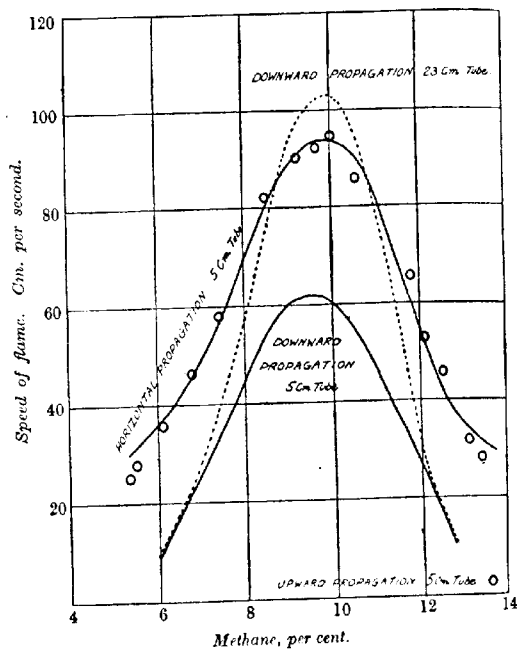
During upward propagation, on the contrary, the initial speeds of the flames should be faster than during the "normal" uniform movement in a horizontal tube, and it would seem unlikely that any phase in the propagation of flame corresponding with the uniform movement would be of long duration.

A glass tube 5 cm. in diameter and 5 m. long was employed for the first series of experiments, with "screen-wires" for recording the speeds of flames stretched across at intervals of 50 cm. Ignition was at a 5 mm. spark-gap 4 cm. from the open end of the tube, and the first screen-wire was stretched at a distance of 20 cm. from the point of ignition. The mouth of the tube was provided with a flange ground to receive an end-piece, which was held in position by metal clips whilst the tube was being filled with the mixture. Before igniting the mixture, this end-piece was slid gently to one side in such a manner as to avoid causing disturbance of the gases within the tube. The method of recording the times of fusion of the screen-wires, and the general mode of procedure for similar experiments, are described in T., 1914, 105, 2609.

As anticipated, the speeds at which the flames travelled downwards were, with all the mixtures employed, uniform over a considerable distance from the point of ignition. A vibratory movement began, in general, somewhat earlier than during horizontal propagation in a tube of the same diameter, but with no mixture was the distance travelled by the flame at a uniform speed less than 100 cm., and with those containing the lower percentages of methane it sometimes exceeded 200 cm.

As regards the magnitudes of the speeds, however, our expectation (based on the assumption that the propagation of flame during the uniform movement in a horizontal tube of small diameter is mainly by conduction of heat) was falsified. In Fig. 1 the results obtained for downward propagation of flame are recorded as a speed-percentage curve for comparison with the curve for the uniform movement in a horizontal tube of the same diameter.

Fig. 1.



Both curves are of the same type, but the speeds of the flames during the initial stage of downward propagation are, over the whole range of inflammable mixtures, but two-thirds the speeds during the uniform movement.

Presumably, then, the transference of heat by convection plays a considerable part in aiding the propagation of flame during the (horizontal) uniform movement even in fairly narrow tubes. This being so, it seemed probable that, contrary to our first assumption, the speed of propagation of flame upwards would be not much, if

any, faster than during horizontal propagation, unless further benefit from convection currents is obtained during the former conditions.

Measurements of the speeds during the upward propagation of flame were not easily made by the method of screen-wires except at or near the limits of inflammability. Over most of the range of inflammable mixtures the flames sometimes began to vibrate violently within 50 or 60 cm. of the open end of the tube. From the moment of ignition, however, the flames, even those that travelled fastest, seemed to move at uniform, or but slightly accelerating, speeds. Attempts were therefore made to measure these speeds, the first screen-wire being placed 10 cm. from the point of ignition and the succeeding wires at distances of 25 cm. from each other. The results were rather irregular. The speed of the flame between the first and second screen-wires was sometimes enhanced by the impetus given by the source of ignition, a distance of travel of 10 cm. being barely sufficient to allow this impetus to die away, and a vibratory movement often began at or before the third screen-wire. However, the measurements were consistent enough to show that over the comparatively short period during which the speed of the flame travelling upwards could be regarded as constant, that speed, for any mixture of methane and air, was not greater than during the uniform movement in a horizontal tube; it was sometimes less.

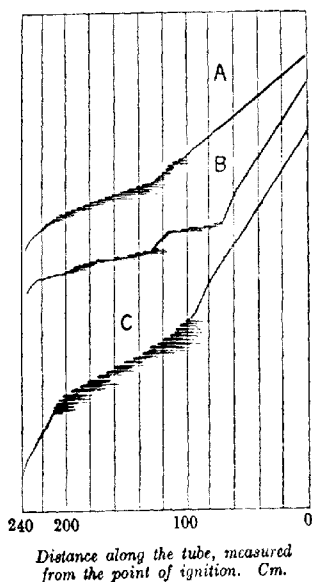
The results are inserted in Fig. 1 as approximate points marked by circles. With the mixtures near the limits of inflammability, such as those containing 5.45, 5.55, and 13.4 per cent. of methane, the flames travelled over a distance of 200–300 cm. at uniform speeds which could be determined accurately, and were distinctly slower than those of the uniform movement in corresponding mixtures in a horizontal tube.

To confirm these results, two series of determinations of speeds of flames in a number of mixtures of methane and air were made by photographing on a rapidly revolving film the illumination of a quartz window in a brass tube 5 cm. in diameter, along which the flames travelled, (1) horizontally, and (2) vertically upwards (see this vol., p. 37). As thus measured, the speeds over the whole range of mixtures were from 3 to 5 cm. per second less when the flames travelled upwards than when they travelled horizontally. Probably this slight difference in the speeds arises from the difference there is in the shape of the flame-front; when travelling horizontally the flame-front has an elliptical cross-section (see T., 1914, 105, 2609, Fig. 2), whereas when travelling upwards it is circular, so that in a tube of given diameter the circumference of

the flame-front relative to its area is greater with an upward- than with a horizontally-moving flame, and the cooling effect of the walls of the tube is correspondingly greater. Since with flames travelling horizontally the length of the major axis of the elliptical flame-front is at its maximum with mixtures near the limits of inflammability, the maximum difference in speed between upward- and horizontally-moving flames in a tube of given diameter should be found with such mixtures. This is so.

Diagrammatic representations of the complete progress of the

FIG. 2.

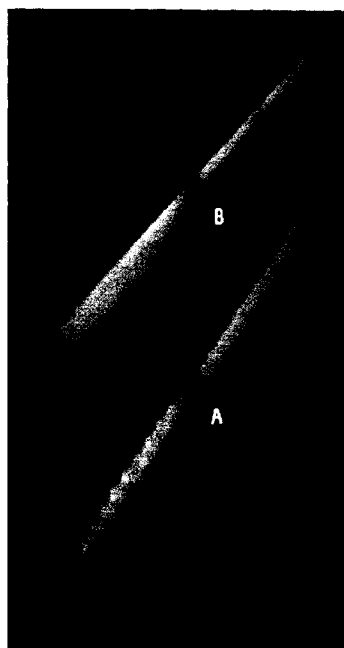


flames travelling in a 10 per cent. mixture of methane and air from end to end (240 cm.) of the brass tube with a quartz window are given in Fig. 2. These diagrams have been reduced in size from tracings taken from the actual photographs, which measured  $60 \times 40$  cm., and were obtained in the manner described in Part I of this research. For the purpose of comparison, the flames should be regarded as travelling from right to left of the diagram and the photographic film as moving vertically upwards; actually, the flame was moving vertically upwards for A, vertically downwards for B, and horizontally for C. The last-named is a tracing

of the photograph reproduced as Fig. 1, Plate I, on p. 66 of this volume. The rate of revolution of the film was not the same for each set of photographs, so that direct comparison of the speeds of the flames cannot be made from the diagrams, which, however, show clearly that the general behaviour of a flame travelling from the open to the closed end of a tube is not dependent on the position of the tube.

We have already commented on the irregularity of some of the results obtained when attempting to measure the initial speeds of the flames by the screen-wire method during upward propagation.





[To face page 1233, Trans.]

The reason for the irregularity under such conditions of experiment became apparent when the movement of the flames was photographed. For it was found that with mixtures containing between 9.0 and 11.0 per cent. of methane the flames were very sensitive to the effect of resonance of the tube, and could acquire either of two speeds (but not speeds intermediate between the two). If resonance was set up in the usual way, by the movement of the flame along the tube, the speed of the flame was normal, but if by some action on the part of the experimenter the tube was caused to resonate at, or very shortly after, the moment of ignition, the mean speed of the flame was 20 cm. per second slower than normal. It has already been observed, and is, in fact, apparent from the photographs and diagrams, that the incidence of resonance retards the general forward movement of the flame until such time as a certain degree of turbulence is imparted to the mixture.

This retarding effect is well illustrated by the photographs reproduced in the Plate, which show the progress of the flame in a 9.7 per cent. mixture of methane and air in the brass tube over the distance 25–55 cm. from the point of ignition, (*A*) when the tube was resonating, and (*B*) when it was not. The photographs were taken within a few minutes of each other on the same film, which was revolving at the same speed in each instance.

Further information as to the difference in character between the two flames was obtained from photographs showing the shape of the flame-front (see Plate). A quartz tube, 5 cm. in diameter, was fixed vertically and covered with black paper except for a slit, 2.5 mm. broad, at right angles to the axis of the tube and 25 cm. from the open end (the lower end), at which ignition was effected. Flames travelling up the tube, in a mixture containing 8.3 per cent. of methane, were photographed, as they passed the slit, on a film which also travelled upwards. As each portion of the flame-front appeared at the slit it was thus photographed on a fresh portion of the film and its shape was recorded. The arrangement of the quartz lens used to focus the slit on the photographic film was such that an image one-quarter the size of the object was obtained; the speed of the film was therefore regulated to be as nearly as possible one-quarter that of the flames, so as to preserve their relative proportions. It will be seen that in *C*, when the tube was resonating, the undulations of the flame-front are well defined and it is unsymmetrical; in *D*, when the tube was not resonating, the flame-front is quite symmetrical.

The important point to have established is that a phase in the propagation of flame during which the speed is uniform is obtained when the flame travels from the open to the closed end of a tube,



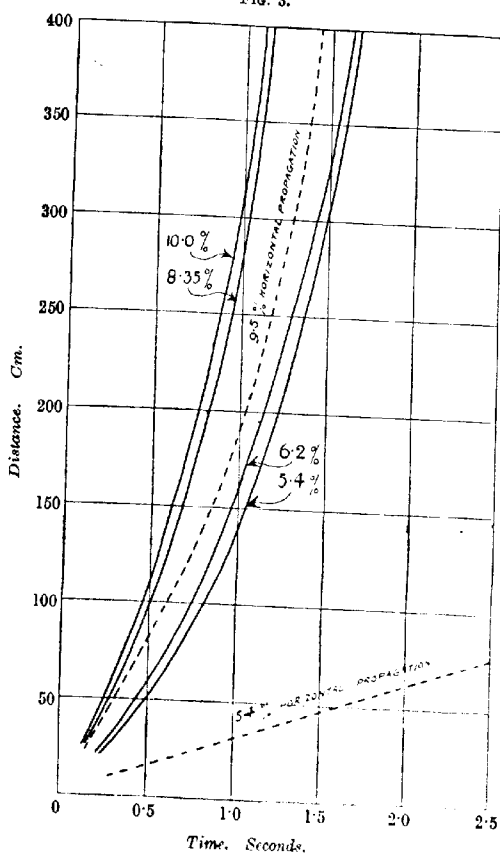
whether the direction of travel is horizontal, vertically upwards, or vertically downwards, and that this uniform speed for any given mixture is slowest during downward propagation. This means that it is not permissible to regard the "uniform movement" (that is to say, the phase of uniform speed of flame during horizontal propagation) as representing "*la vitesse normale de propagation de la flamme par conductibilité.*" If propagation of flame solely by conduction of heat obtains at all, our experiments show that it is most likely to occur when the flame travels downwards, the effect of convection currents being assumed then to be negligible.

When travelling downwards in a glass tube 5 cm. in diameter, the flame-front during the period of uniform speed of propagation of flame is, with all mixtures of methane and air, a steady, or but gently undulating, disk. There is no suspicion of turbulence such as makes its appearance with the more rapid flames when they travel horizontally in such a tube. It seemed possible, therefore, that, if convection currents do not materially assist the flame in its propagation downwards, a considerable increase in the diameter of the tube down which the flames travel could be made without their speeds being augmented. On trial, however, using a metal tube 23 cm. in diameter and 7 m. long, it was found that with mixtures containing more than 7 and less than 12 per cent. of methane the speeds of the flames were considerably greater than in a glass tube 5 cm. in diameter, as the curve in dotted line in Fig. 1 shows. With the mixtures containing between 9 and 11 per cent. of methane, the ratio between the speed of the flame and the diameter of the tube was nearly the same as when the flames travel horizontally (see Fig. 3, T., 1917, 111, 1052). However it may be during the downward propagation of flame in mixtures containing less than 7 or more than 12 per cent. of methane, it is obvious, therefore, that something other than conduction of heat is responsible for the development of the more rapidly moving flames in the tube of larger diameter. The enhanced speeds of the flames as they travel downwards in the larger tube are no doubt due to turbulence of the flame-front engendered by convection or eddy currents.

We can, then, fully endorse Schloessing and de Mondésir's statement that the normal propagation of flame is rarely observed when the word "normal" is taken to imply "by conduction of heat." It is highly abnormal that such a mode of heat transference should alone be operative during the propagation of flame. In so far, therefore, as the term "uniform movement" of flame has been held to be the normal propagation of flame by conduction of heat, it ought to be discarded. The term is, however, a useful

one, and fittingly describes a phase in the propagation of flame (obtainable under a variety of conditions, which should be specified) the identification and measurement of which is of considerable

FIG. 3.



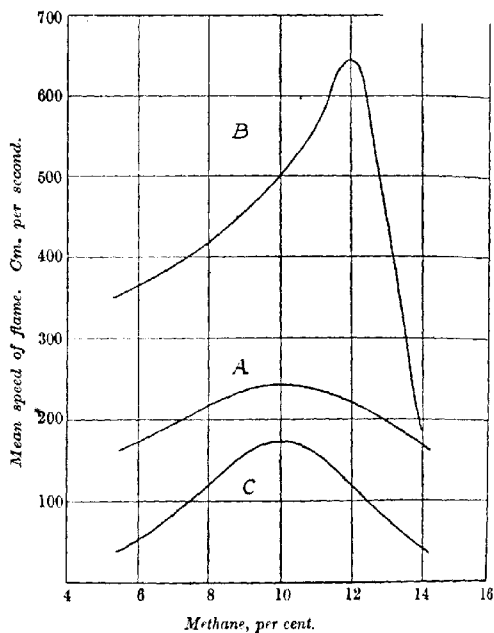
value. As a name, without implying a mode of heat transference during the phenomena it describes, there is no reason why it should not be retained, and it may be convenient to do so.

## II. Ignition at One End of a Vertical Tube Open at both Ends.

—Under these conditions, the tube in which the flame travels

becomes a "chimney," and there is added to the speed of a flame travelling up the tube the speed of the draught produced by the chimney. In addition, the mechanical effect of this draught in promoting turbulence of the mixture probably augments the speed of the flame. Flame does not pass downwards if the mixture is ignited at the top of the tube, but continues to burn at the mouth until the whole of the mixture has been drawn up.

FIG. 4.



In Fig. 3 are shown time-distance curves for the propagation of flame upwards in several mixtures of methane and air in a vertical glass tube 5 cm. in diameter and 5 m. long, open at both ends. These curves should be compared with those obtained when the tube was horizontal (Fig. 1, this vol., p. 42). The character of both sets of curves is similar, and indicates a gradual and regular acceleration of speed as the flame travels from end to end of the tube. This acceleration occurs with the lower-limit mixture (54

per cent. of methane) when the flame travels upwards, a result which displays clearly the chimney effect of the tube, for the speed of the flame in the lower-limit mixture is quite uniform when it travels horizontally.

The speeds of the flames at all stages of their propagation are considerably faster during upward than during horizontal propagation, for the reasons already given. Fig. 4 records the mean speeds over measured distances for the whole range of inflammable mixtures: (A) for the distance 50–100 cm. measured from the first screen-wire, which was 10 cm. from the point of ignition, and (B) for the distance 200–300 cm. A curve (C) showing the mean speed over the distance 50–100 cm. during horizontal propagation in the same tube is given for comparison.

Curve B presents a characteristic novel to these investigations on the propagation of flame in mixtures of methane and air, inasmuch as the maximum speed of flame is found, not, as is usual, with mixtures containing between 9.5 and 10.5 per cent. of methane, but with those containing about 12 per cent. This result, which is, of course, due to the chimney effect of the tube, is probably quite adventitious; with the particular diameter and length of tube employed, the chimney effect assumed a maximum with mixtures containing about 12 per cent. of methane, perhaps by reason of the composition of the products of combustion of those mixtures.

III. *Ignition at the Closed End of a Vertical Tube Open at the other End.*—When the mixture is ignited at the closed end of a tube open at the other end, the position of the tube does not affect the results. The results obtained when the tube is horizontal have been described in Part I.

### PART III.—THE PROPAGATION OF FLAME IN CURRENTS OF MIXTURES OF METHANE AND AIR.

The object of these experiments was: (i) to determine whether the fact that the gases were moving as a current would simply add to the speed of the flame the speed of that current, or whether an effect of turbulence would be introduced, and (ii) to see if a smaller quantity of methane than that which forms the lower-limit mixture (5.4 per cent. for horizontal or upward propagation of flame) in a still atmosphere would be capable of conveying flame from one place to another if the mixture itself were moving.

(i) The experiments with a vertical tube open at both ends, described in Part II of this research, had shown that the speed of

the current induced in such a tube, acting as a chimney, was added to the speed of a flame travelling upwards in it, and it was assumed that turbulence caused by the current further increased the speed of the flame, though no proof of this could be given, since the velocity of the current was indeterminate.

A tube 2.5 cm. in diameter and 220 cm. long was fixed horizontally and connected by rubber tubing to a large metal gas-holder, a short brass tube with a disk of metal gauze at either end being interposed to prevent flame travelling back into the holder. Streams of a mixture of methane and air could be caused to pass at different speeds along the tube, both ends of which were open, by varying the counter-weights on the bell of the holder and opening the wide-bore metal tap thereon to its full extent. The mixtures were ignited electrically at a point 26 cm. from the connexion to the brass tube, and the speeds of the flames were measured by means of screen-wires, the first screen-wire being 50 cm. from the point of ignition.

A mixture containing 6.35 per cent. of methane was used, as being one in which the speed of flame in a still atmosphere under the conditions of the experiments would not be excessive in comparison with that of the currents that could be produced. The results, giving the mean speeds of the flames over 100 cm., were as follow:

Speed of current. Cm. per second.	Speed of flame. Cm. per second.	Difference. Cm. per second.
Nil	287	287
23	582	559
43	952	909
75	1527	1452

It is thus apparent that the major effect of the current is that of turbulence. The fact that such a comparatively gentle movement of the mixture as is represented by a speed of 23 cm. per second should nearly double the speed of the flame is very striking and emphasises the important part that convection currents must play in the transmission of flame.

(ii) When a homogeneous mixture of methane and air containing between 4 and 5 per cent. of methane is caused to travel slowly over a small flame, such as that of a candle, flares of flame of burning methane are produced which follow the direction of the current, and may extend for a considerable distance—a distance greater than the length of the "cap" produced by a similar mixture around such a flame in a still atmosphere. These flares of burning methane may even become detached from the source of heat around which they form and float away for a short distance in the stream of mixture (T., 1914, 105, 2594).

We had also obtained evidence that if a sufficient degree of turbulence is produced in a closed vessel, by means of a rapidly revolving fan, in a mixture of methane and air containing not less than 5.0 per cent. of methane, flame will travel throughout the mixture, following the current induced by the fan (T., 1914, 105, 2595). Since the effect of causing a mixture of methane and air to travel along a tube at a fairly slow speed is to impart turbulence to the mixture, and since the degree of turbulence thus imparted is sufficient greatly to increase the speed of propagation of flame in (that is to say, the rate of combustion of) the mixture, it seemed probable that the lower limit of inflammability, which is partly dependent on the rate of combustion of the gas, might be less with a slow stream of methane and air than with a quiescent mixture, just as the lower limit is less for upward propagation of flame (5.4 per cent.), when the combustion is aided by convection currents, than for downward (6.0 per cent.).

A horizontal glass tube 5 cm. in diameter and 320 cm. long was used for the experiments, which were conducted in a similar manner to those already described. The point of ignition was 17 cm. from the brass tube connecting the glass tube to the gas-holder, and the first screen-wire was 35 cm. from the point of ignition. The experiments were as follow:

(a)  $\text{CH}_4$ , 5.15 per cent.—Speed of current, 65 cm. per second. A flame, about 2.5 cm. long, travelled the whole length of the tube occupying the upper half of it. The speed of the flame increased gradually over the last 200 cm. from 75 to 85 cm. per second.

(b)  $\text{CH}_4$ , 5.10 per cent.—Speed of current, 65 cm. per second. Observations as in previous experiment, the speed of the flame being about 70 cm. per second throughout.

(c)  $\text{CH}_4$ , 5.05 per cent.—Speed of current, 65 cm. per second. A more powerful secondary discharge had to be used to ignite this mixture. The flame produced was only 1.2 cm. long, but it travelled the whole length of the tube at a speed of 65 cm. per second—that is to say, at the speed of the current of mixture.

(d)  $\text{CH}_4$ , 5.02 per cent.—The intense "flaming" discharge obtained when a Wahnelt electrolytic interrupter is used in the primary circuit of an induction coil had to be used to ignite this mixture. When ignited, a small flame travelled throughout the length of the tube at the speed of the current of mixture, namely, 65, 50, and 35 cm. per second in successive trials. With a faster speed of current (about 80 cm. per second) or a slower speed (about 30 cm. per second), the flame travelled from 200 to 250 cm. and then died out.

(e)  $\text{CH}_4$ , 5.00 per cent.—With no speed of current would flame travel more than about 50 cm. from the point of ignition. This was so whether the Wehnelt discharge used to ignite the mixture was maintained or passed momentarily.

Experiments (d) and (e) were repeated many times, with the same results: a mixture containing 5.02 or 5.03 per cent. of methane does not enable flame to travel in it when it is at rest, but when it is moving as a current along a tube, flame travels in it at the speed of the current. A mixture containing 5.00 per cent. of methane could not be caused to propagate flame under the conditions of the experiments. Mixtures containing 4.95, 4.90, or 4.85 per cent. of methane gave flares of flame extending a few cm. only along the tube.

The scale on which these experiments were conducted is perhaps scarcely sufficient to warrant the conclusion that flame would be carried indefinitely in a homogeneous mixture containing 5.02 per cent. of methane, along the roadway of a mine, for example, so long as a current of from 35 to 65 cm. per second was maintained. The general character of the experiments, however, pointed to a sharp distinction between a mixture (5.00 per cent. methane) obviously incapable of maintaining a flame apart from the source of heat which originated it, and one (5.02 per cent. methane) in which flame was maintained after the igniting source had been withdrawn. The flame would travel along the roof of the roadway.

The concluding parts of this research will deal generally with the effects of turbulence on the propagation of flame in mixtures of methane and air, as produced by the passage of the mixtures as currents along a tube or gallery, and as induced locally by the presence of restrictions in the gallery.

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[Received, August 21st, 1920.]

CXXXIV.—*The Oxidising Properties of Sulphur Dioxide. Part II. Iron Phosphates.*

By WILLIAM WARDLAW, SIDNEY RAYMOND CARTER, and  
FRANCIS HERBERT CLEWS.

THE object of the experiments described in the present communication was to determine whether the oxidising action of sulphur dioxide exhibited in concentrated hydrochloric acid solution (Wardlaw and Clews, this vol., p. 1093) was restricted to this acid or was operative in other acid solutions. Phosphoric acid was selected on account of its non-volatility, and its consequent suitability for quantitative measurements.

## EXPERIMENTAL.

*Experiment with Ferrous Phosphate Solution.*

Solutions of ferrous phosphate were prepared by dissolving iron in phosphoric acid (Erlenmeyer, *Annalen*, 1878, **194**, 182) and treating with sulphur dioxide. Essentially, therefore, the method of procedure was practically identical with that previously employed for the investigation of ferrous chloride reactions (*loc. cit.*). As illustrative of the method used, the following details of the first experiment may be given.

One gram of pure iron was dissolved in 50 c.c. of phosphoric acid (D 1.75, 89 per cent.  $H_3PO_4$ ) contained in a closed flask, a stream of carbon dioxide being continually passed through the apparatus. A colourless solution of ferrous phosphate was thus obtained. The evolution of hydrogen having ceased, sulphur dioxide was passed through the solution at  $115^\circ$ . After about ten minutes, a faint milkiness was seen in the neck of the flask, and in the course of time, particles of sulphur appeared. The solution remained colourless throughout. After the sulphur dioxide had passed for four hours, the gas was removed from the solution by the passage of carbon dioxide. The ferrous and total iron were determined by titration with potassium dichromate solution. The first experiment showed that 8.1 per cent. of ferric phosphate had been formed under the conditions mentioned. In view of the extreme susceptibility of ferrous phosphate to atmospheric oxidation (Erlenmeyer, *loc. cit.*), the oxidation by sulphur dioxide was not unexpected.



*Experiments with Ferric Phosphate Solutions.*

To determine whether sulphur dioxide had any reducing action on ferric phosphate, 3 grams of ferric phosphate were dissolved in 50 c.c. of glacial phosphoric acid, and sulphur dioxide was passed through the solution, maintained at  $115^{\circ}$ , for three hours. On analysing the solution, no ferrous iron could be detected. Further experiments on similar lines gave no evidence of reduction of the ferric phosphate. This result seems to agree with the well-known stability of ferric phosphate in the reducing blowpipe flame. A borax bead containing ferric iron is readily reduced, whereas a ferric microcosmic bead is reduced with difficulty.

*Experiments with Ferrous-ferric Phosphate Solutions.*

The object of these experiments was to determine whether the prolonged action of sulphur dioxide on ferrous phosphate would result in complete oxidation to the ferric state. The mixtures were made by dissolving iron in phosphoric acid, excluding air during the process, and adding a solution of ferric phosphate in concentrated phosphoric acid.

Concentration of iron: approximately 1 gram per 50 c.c. of solution.

Duration of experiments: four hours.

TABLE I.

Temperature,  $115^{\circ}$ .

Ferrie iron. Per cent.		Sulphur deposit.
Initial.	Final.	
0.0	8.1	Heavy.
12.5	15.7	Moderate.
21.9	24.7	Moderate.
25.0	28.0	Moderate.
39.7	—	Very light.
55.7	56.9	Just noticeable.
100.0	100.0	None.

TABLE II.

Temperature,  $150^{\circ}$ .

Ferrie iron. Per cent.		Sulphur deposit.
Initial.	Final.	
43.2	45.7	Moderate.
57.1	60.5	Moderate.
63.4	65.2	Light.
72.0	74.2	Light.
79.1	79.9	Just noticeable.
100.0	100.0	None.

The presence of the great excess of phosphoric acid tended to make the titration somewhat difficult, but the character of the sulphur deposit served as a good indication of the progress of oxidation, especially in those cases where it occurred only to a slight extent.

Comparison of the results obtained at the two temperatures suggests that ferrous phosphate would be completely oxidised to

the ferrio state, but that at the temperatures used in these experiments the velocity of reaction is becoming slow, with increasing proportion of ferrio salt. Hence during the four hours very little oxidation is detected with the higher proportions of ferrio iron.

*Limit of Oxidation of Ferrous Phosphate.*

Experiments to determine the limit of oxidation were carried out in a special apparatus primarily designed for obtaining the velocity of reaction. The reaction vessel consisted of a wide-necked flask of about 600 c.c. capacity fitted with a rubber stopper, through which passed the bearing for a stirrer, a syphon sampling-tube made of capillary tube of fairly wide bore, an inlet tube for the sulphur dioxide, and a water-cooled exit tube. The syphon sampling-tube was connected with a water-cooled 10 c.c. burette, which in turn was connected with a suction pump. The stirrer was fitted with a mercury seal and closed at the end, so that sulphur dioxide could be maintained at a slight pressure in the flask without leakage. A simple device was used to control the pressure of sulphur dioxide in the flask. The gas issuing from a sulphur dioxide syphon was divided by a T-piece, one arm being connected with the reaction flask and the other connected with a gauge-tube containing concentrated sulphuric acid. By allowing the sulphur dioxide to bubble very slowly through the sulphuric acid, the pressure in the reaction flask was maintained at a value greater than atmospheric, the excess pressure being proportional to the height of the sulphuric acid column.

*Method of Procedure.*—To 250 c.c. of phosphoric acid contained in the flask was added a definite weight of pure iron. A current of carbon dioxide was then passed through the apparatus, and, on warming, the iron dissolved. When solution was complete, the temperature of the thermostat was adjusted to 150°, and the stream of carbon dioxide replaced by one of sulphur dioxide. By closing the exit tube, the pressure of sulphur dioxide was adjusted. Samples of solution were periodically drawn off into the burette, allowed to cool to the ordinary temperature, the volume adjusted, and run into a flask filled with carbon dioxide. The solution was then diluted with 30 per cent. phosphoric acid, and the sulphur dioxide driven off. The volume was made up to 100 c.c. and titrated with  $N/20$ -potassium permanganate. The titre was assumed to be proportional to the concentration of ferrous iron in the reaction flask at the moment of sampling.

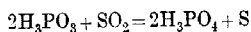
From experiments conducted in this way, a constant ferric content was found to be established at the end of from two to three days, and the following were the results obtained:

(a) At a concentration of 7.35 grams of iron per 250 c.c. of phosphoric acid, the mixture contained 36 per cent. of ferric iron.

(b) At a concentration of 3.65 grams per 250 c.c., the mixture contained 45 per cent. of ferric iron.

These results differ distinctly from those obtained from the synthetic mixtures of ferrous and ferric phosphates. This difference might conceivably be due to the sulphur formed in the solutions containing initially only ferrous phosphate, which is absent in the case of the synthetic mixtures. Experiments with synthetic mixtures of ferrous and ferric phosphates to which had been added finely divided or colloidal sulphur showed that this had no observable effect on the degree of oxidation by sulphur dioxide. In addition, sulphur was found to have no appreciable reducing power on ferric phosphate in concentrated phosphoric acid solution.

Maquenne (*Bull. Soc. chim.*, 1890, [iii], **3**, 401) has shown that aqueous solutions of phosphorous acid are oxidised by sulphur dioxide completely to phosphoric acid (compare also Wöhler, *Annalen*, 1841, **39**, 252, and Cavazzi, *Gazzetta*, 1886, **16**, 169). The possibility of the reaction



being reversible was not overlooked, but experiments did not confirm this conjecture.

*Velocity and Order of Reaction.*—Experiments made with the apparatus described above with a view to determine the rate and order of reaction gave no very definite results, probably owing to the disturbing action of sulphur.

*Limiting Concentration of Phosphoric Acid.*—This has been determined between narrow limits for ferrous phosphate at 100°. The procedure followed was similar to that used in the case of hydrochloric acid solutions (Wardlaw and Clews, this vol., p. 1097). One gram of iron was dissolved in 50 c.c. of phosphoric acid of different concentrations, the values for which were obtained by measuring the specific gravity of the phosphoric acid and calculating the concentrations from the tables (Hager, "Kommentar zur Pharmacopœa Germanica"; Gmelin-Kraut's "Handbuch," Vol. I, Pt. 3). The results are shown in table III.

A gravimetric estimation was made on the solution in expt. 6 according to Finkener's method (*Ber.*, 1878, **11**, 1640), and it was shown to contain 400.7 grams of phosphoric acid per litre. whilst 32.83 per cent. phosphoric acid (expt. 6) contains 397.2 grams per litre. Assuming the iron to be in combination as  $\text{Fe}(\text{H}_2\text{PO}_4)_2$  (Erlenmeyer, *loc. cit.*), the free acid in 1 litre of the ferrous phosphate solution was  $400.7 - 68.6 = 332.1$  grams.

TABLE III.

Concentration of iron: 1 gram per 50 c.c.

Temperature: 100°.

Duration of experiments: four hours.

Experiment:	1.	2.	3.	4.
Concentration of $H_3PO_4$ , per cent. ....	76.27	45.93	40.87	37.17
Oxidation, per cent. ....	2.1	1.3	1.0	—
Observations .....	sulphur.	sulphur.	sulphur.	sulphur.

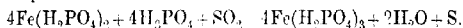
  

Experiment:	5.	6.	7.	8.
Concentration of $H_3PO_4$ , per cent. ....	34.38	32.83	31.80	20.02
Oxidation, per cent. ....	—	—	—	—
Observations .....	Minute amounts.	Very minute deposit.	No deposit.	No deposit.

It is concluded, therefore, that oxidation of ferrous phosphate by sulphur dioxide is just perceptible in a solution containing 332.1 grams of "free" phosphoric acid per litre at 100°.

#### Discussion of Results.

The reactions of sulphur dioxide with iron phosphates in the presence of concentrated phosphoric acid differ in several ways from those with iron chlorides in concentrated hydrochloric acid solution. In the first place, there is no evidence that sulphur dioxide can act as a reducing agent in the presence of concentrated phosphoric acid, for ferric phosphate, unlike ferric chloride, in the presence of the corresponding concentrated acid, is not affected by the action of sulphur dioxide. The reaction between sulphur dioxide and iron phosphates in concentrated phosphoric acid solution is therefore solely one of oxidation, and may be expressed by the equation

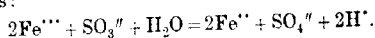


The question now arises as to whether the reaction is a reversible one, like the corresponding ferrous chloride reaction, or whether it proceeds to completion. The fact that mixed ferrous-ferric phosphate solutions gave evidence of oxidation with relatively large percentages of ferric salt rather seems to indicate that the reaction would ultimately proceed to completion. This idea also seems to be supported by the non-reducibility of ferric phosphate by sulphur. Against this conception, however, must be placed the limited yield of ferric salt from an initially pure ferrous phosphate solution and the favourable influence of the concentrated phosphoric acid on the oxidation. Both these facts would be deduced

from the law of mass action if applied to the above equation, taking it as representing a reversible reaction. Undoubtedly, the complicating feature in the reaction is the formation of the stable complex compound which ferric phosphate is known to form with phosphoric acid. This would account for the greater yield of ferric salt from a pure ferrous phosphate solution than from a pure ferrous chloride solution, owing to the fact that the ferric salt formed would be removed from the reaction in the form of the stable complex compound, and hence favour the degree of oxidation. This formation of the complex salt may also account for the non-reducibility of the ferric phosphate in concentrated phosphoric acid solution by the action of sulphur. It is quite conceivable that sulphur may reduce ferric phosphate when not in the form of the complex compound. Such conditions are probably present when sulphur dioxide is passed into a pure ferrous phosphate solution. The sulphur liberated is in a very active state and may react with the ferric phosphate generated before it is taken up in the form of the complex. A consideration of these factors incline the authors to the idea that the reaction of sulphur dioxide with ferrous phosphate is a reversible one similar to that of sulphur dioxide with ferrous chloride in the presence of their corresponding concentrated acids, but that it is modified in the case of the ferrous phosphate by the formation of the complex stable compound which ferric phosphate forms with phosphoric acid.

The facts that sulphur dioxide reduces most readily in a very dilute acid medium, and that it oxidises most readily in a strong acid medium, may be correlated if oxidation and reduction are explained on an ionic basis, oxidation being represented by the surrender of positive charges and reduction by the transference of negative charges.

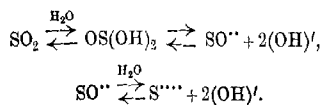
Sulphur dioxide in aqueous solution is generally regarded as a moderately weak acid ionising principally into  $H^+$ ,  $HSO_3'$ , and  $SO_3''$  ions. It is in this condition that it reacts as a reducing agent. Thus:



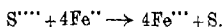
In strongly acid solution containing a large number of hydrons, the concentration of  $SO_3''$  ions will be reduced, and, on the above assumption, its power of reducing should be diminished. This is in accordance with experimental results.

Now let it be assumed that sulphur dioxide is capable of ionising to an extremely minute extent as a base, yielding a correspondingly minute amount of sulphur ions. It has been shown that the sulphoxides, the organic analogues of sulphur dioxide, have

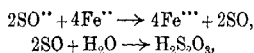
basic properties (Fromm and Raiziss, *Annalen*, 1910, **374**, 90; Fromm, *ibid.*, 1913, **396**, 75). This tendency will be all the greater the larger the number of hydrions present in solution. Thus:



In view of the large number of hydrions present in the solution, the concentration of hydroxyl ions would be reduced to a very low value and the reaction towards the right favoured. Oxidation is now represented:



If oxidation takes place due to the ion  $\text{SO}''$ ,



which represents an intermediate stage in the reduction of sulphur dioxide to sulphur. Thiosulphuric acid would break up into sulphur dioxide and sulphur. It may be observed that the latter hypothesis is in many respects a re-statement of the thionyl chloride hypothesis (Wardlaw and Clews, this vol., p. 1103) applied ionically and more generally.

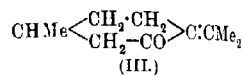
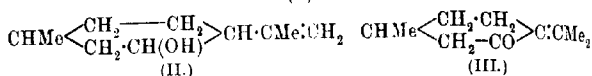
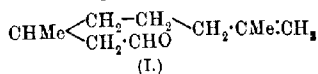
The oxidising properties of arsenic acid, uranyl chloride, permanganic acid, and chromic acids have been explained by Stieglitz ("Qualitative Chemical Analysis," Vol. I, p. 282 *et seq.*) on a similar assumption.

There appears to be room for investigation of these reactions from the point of view of electrical potentials when some of the assumptions made in the above could be tested, and it is hoped that experiments now in progress may throw some further light on this hypothesis.

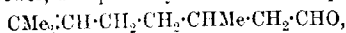
CXXXV.—*The Alcohols of the Hydroaromatic and Terpene Series. Part III.\* isoPulegol.*

By ROBERT HOWSON PICKARD, HAROLD HUNTER, WILLIAM LEWCOCK, and HANNAH SMITH DE PENNINGTON.

TIEMANN and Schmidt (*Ber.*, 1896, **29**, 914) obtained the alcohol isopulegol (II) by the hydrolysis of the condensation product of acetic anhydride and citronellaldehyde (I). The product was so named to distinguish it from the yet unknown isomeric secondary alcohol, which would correspond with the ketone, pulegone (III).



Samples of citronellaldehyde often vary considerably in optical dextrorotatory power, and probably contain the compound,



as well as that of formula I (see, *inter alia*, Prins, *Chem. Weekblad*, 1917, **14**, 692).

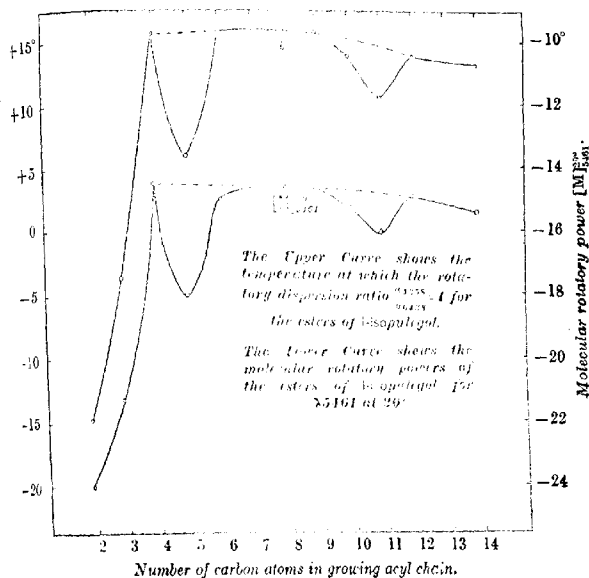
Our preparations of isopulegol from the same sample of aldehyde ( $[\alpha]_D^{20} + 11.6^\circ$ ) by the method described by Tiemann and Schmidt, or by the modifications of the same proposed by Semmler (*Ber.*, 1909, **42**, 2014) and by Wegscheider and Späth (*Monatsh.*, 1910, **30**, 825), gave isopulegol of rotatory power  $[\alpha]_D^{20} \pm 2^\circ$ . In no case, however, did these products yield, after oxidation with chromic acid, any ketone forming a bisnitroso-derivative so characteristic of pulegone and similar  $\alpha\beta$ -unsaturated ketones (compare Baeyer and Heinrich, *Ber.*, 1895, **28**, 654). During the condensation, and due to the formation of the cyclohexane ring, two additional carbon atoms become asymmetrical, so that four stereoisomeric pairs of dextro- and laevo-rotatory compounds of the formula ascribed above to isopulegol are theoretically possible. The nomenclature for such isomerides proposed by Aschan, and used in Part II for the menthols, is inconvenient here, as it would necessitate the use of the prefix *iso* twice over, so the isopulegols may be here simply described as isopulegol,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isopulegols, as it is not yet possible to determine the configurations of the respective isomerides.

A detailed investigation of the mixtures of isopulegols, obtained

\* Part I., T., 1907, **91**, 1973. Part II., T., 1912, **101**, 109.

from the condensation of dextrorotatory citronellaldehyde, has now shown that two (and probably not more) of the four possible\* isomerides are formed, and as the yield of the isopulegyl acetates rarely amounts to 50 per cent., it is probable that the aldehyde taking part in the condensation is the pure dextrorotatory compound of formula I. The hydrogen phthalic esters of the mixture of alcohols obtained from the condensation product can be separated by the fractional crystallisation of the magnesium† and

FIG. 1.



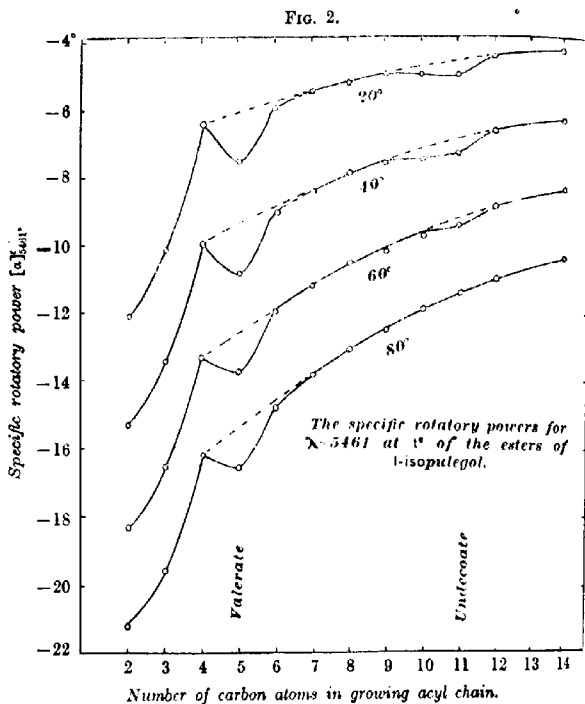
strychnine salts. In this manner, starting from *d*-citronellaldehyde, the esters of *l*-isopulegol and *d*- $\alpha$ -isopulegol have been isolated, and it has been found that the two alcohols, when reduced, yield respectively *l*-menthol and *d*-neo-menthol, both of which, when oxidised, give *l*-menthone (Part II). The analogy of these cases to that of *d*-borneol and *l*-isoborneol, which, as shown in Part I, both correspond with *d*-camphor, is very striking, whilst Tschugaev (*Ber.*, 1912, 45, 1293) has shown that tanaetone, when

\* That is, assuming no racemisation takes place during the condensation.

† Both magnesium salts are dextrorotatory in ethyl-alcoholic solution.



reduced, forms two tanacetyl alcohols of different configuration and opposite in rotatory power. It would appear that, in general, the reduction of an optically active cyclic ketone to the corresponding secondary alcohol yields a mixture of the two possible *cis*- and *trans*-isomerides of opposite rotatory powers. In this connexion, further analogies may be mentioned, as Aschan has described (*Annalen*, 1901, **316**, 196) the conversion of *d*-camphoric

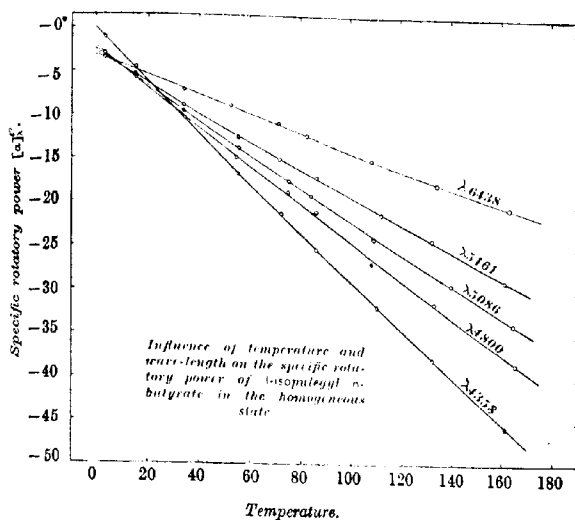


acid (the *cis*-isomeride) into *l*-isocamphoric acid (the *trans*-isomeride), and Forster (T., 1898, **73**, 386) the formation of dextro-rotatory bornylamine and levorotatory *neobornylamine* from *d*-camphor.

The values obtained for the optical rotatory power for  $\lambda 4358$  to 6438 of *l*-isopulegol in the homogeneous state at  $20^\circ$  correspond with a one-term Drude equation almost to within the experimental error, but at higher temperatures they do not. The rotatory

powers of its esters with the normal fatty acids offer a strong contrast to those of the esters of *l*-menthol. Thus in the homologous series their molecular rotatory powers tend to a constant value only at higher temperatures (see table I), and do not in the homogeneous state at any temperature from 10° to 160° agree with a one-term Drude equation, being visibly anomalous in dispersive power at the ordinary temperature (see, for example, Fig. 3). Further, when plotted against molecular weight, the specific rotatory powers, unlike those of the menthyl esters, show

FIG. 3.



maxima (more prominent at the lower temperatures, see Fig. 2) for the valerate and undecate, that is, when the growing chain may be assumed to return on itself. In ethyl alcoholic solution there are, in addition, indications of irregularities in such a curve at the propionate and octoate.\*

The special positions of the valerate and undecate on this curve are well illustrated in Fig. 1, which also shows the same phenomenon in the curve drawn to connect molecular weight and the temperatures (extrapolated, where necessary, from observations

\* Compare in this connexion somewhat similar phenomena in the rotations of the esters of *d*-1-naphthyl-*n*-hexylcarbinol (Pickard and Kenyon, T., 1914, 105, 2644).

given on p. 1256), at which the esters have a dispersion ratio equal to unity for  $\lambda$  6438 and 4358. The rotatory powers are given in the tables, but further discussion of these and similar results obtained by one of us and Kenyon (T., 1914, 105, 830 *et seq.*), or of the criticism by Frankland and Garner (T., 1919, 115, 639) of the tentative hypothesis adopted to explain them, is postponed until further evidence is available. The variation of the specific rotatory powers of the esters with temperature from 10° to 180° is nearly linear (illustrated in Fig. 3 for the butyrate), and should be considered along with similar results obtained by Kenyon (T., 1914, 105, 2226) in view of the suggestions of Patterson (T., 1913, 103, 156).

TABLE I.

*Molecular Rotatory Powers of l-isoPulegol and its Esters in the Homogeneous State.*

	$[M]_{4358}^{20^\circ}$	$[M]_{4358}^{25^\circ}$	$[M]_{4358}^{30^\circ}$	$[M]_{4358}^{35^\circ}$
<i>l-isoPulegol</i> .....	-28.1°	-29.9°	-66.3°	-72.2°
Acetate .....	18.8	31.0	30.7	61.9
Propionate .....	17.2	30.1	25.6	61.0
<i>n</i> -Butyrate .....	12.4	26.6	14.1	52.4
<i>n</i> -Valerate .....	14.9	29.0	20.5	57.4
<i>n</i> -Hexoate .....	13.1	27.9	14.7	54.1
<i>n</i> -Heptoate .....	12.9	27.1	14.6	53.2
<i>n</i> -Octoate .....	12.9	27.4	14.7	53.4
<i>n</i> -Nonoate .....	12.8	27.1	14.5	53.3
<i>n</i> -Decoate .....	12.8	27.8	15.9	53.5
<i>n</i> -Undecoate .....	13.9	27.8	17.8	53.0
<i>n</i> -Dodecoate .....	12.9	27.9	15.6	53.5
Myristate .....	13.9	28.4	16.3	54.7

## EXPERIMENTAL.

*Isolation of l-isoPulegol.*

The mixture (b. p. 82—90° 10 mm.) of alcohols (obtained by the hydrolysis of the condensation product of citronellaldehyde,  $[\alpha]_D +11.6^\circ$ , and acetic anhydride) is heated in an oil-bath at 110° for twelve hours with an equimolecular amount of phthalic anhydride. The product is dissolved in a very dilute cold aqueous solution of sodium carbonate, which is then carefully extracted with ether to remove neutral compounds. Any dissolved ether is removed by a current of air, and then the solution precipitated with the calculated amount of a solution of magnesium chloride. The resulting pasty mass is strained off and crystallised eight times from alcohol containing some water, which is diminished as the separation nears completion. By working up the mother liquors (a) by concentration of the alcoholic solutions, and (b) by recovery

of the hydrogen phthalic esters from the more soluble fractions and re-working these as before, a yield of just over 40 per cent. of the magnesium salt of *l*-isopulegyl hydrogen phthalate is obtained.

*Magnesium l-isopulegyl phthalate* crystallises from aqueous alcohol in lustrous flakes with  $6\text{H}_2\text{O}$  (Found:  $\text{Mg}=3.3$ ;  $\text{H}_2\text{O}=14.3$ .  $\text{C}_{36}\text{H}_{42}\text{O}_8\text{Mg}\cdot 6\text{H}_2\text{O}$  requires  $\text{Mg}=3.3$ ;  $\text{H}_2\text{O}=14.6$  per cent.), which melt at  $111^\circ$  and are soluble in chloroform or acetone. It has  $[\alpha]_{\text{D}}^{25} +7.8^\circ$ ,  $[\alpha]_{\text{D}}^{30} +18.2^\circ$ ,  $[\alpha]_{\text{D}}^{35} +23.2^\circ$ ,  $[\alpha]_{\text{D}}^{40} +30.3^\circ$ , and  $[\alpha]_{\text{D}}^{45} +57.4^\circ$  in alcohol ( $c=5$ ) at  $20^\circ$ . It is decomposed by cold hydrochloric acid, which precipitates *l*-isopulegyl hydrogen phthalate. This ester crystallises from glacial acetic acid in stout prisms, which melt at  $106^\circ$ . It has  $[\alpha]_{\text{D}}^{25} -19.39^\circ$ ,  $-25.77^\circ$ ;  $[\alpha]_{\text{D}}^{30} -23.55^\circ$ ,  $-31.91^\circ$ ;  $[\alpha]_{\text{D}}^{35} -28.59^\circ$ ,  $-39.10^\circ$ ;  $[\alpha]_{\text{D}}^{40} -33.44^\circ$ ,  $-37.55^\circ$ ; and  $[\alpha]_{\text{D}}^{45} -53.32^\circ$  and  $-75.58^\circ$  in alcohol and benzene respectively ( $c=5$ ) at the temperature of the laboratory.

The *strychnine* salt crystallises from absolute alcohol in long, prismatic needles, which melt at  $205^\circ$ . The homogeneity of the ester was inferred from the constancy of its levorotation in alcohol and chloroform (i) after an attempted fractional crystallisation from acetic acid, and (ii) after conversion into the strychnine salt, which was repeatedly recrystallised, and its recovery.

*l*-isopulegol is obtained by the hydrolysis of the hydrogen phthalate with an excess of sodium hydroxide dissolved in ethyl alcohol. It boils at  $88^\circ/10$  mm., and its rotatory power is unaltered by partial esterification with either phthalic or acetic anhydride, the unesterified isopulegol and that obtained from the hydrolysis of the esters having identical rotations. When suspended in water containing 10 per cent. of gum arabic in the presence of colloidal palladium, it is reduced rapidly by hydrogen to a crystalline solid (m. p.  $42^\circ$  and  $[\alpha]_{\text{D}}^{25} -49.4^\circ$ ) identical with *l*-menthol.

*d*-isopulegol.—The more soluble component obtained in the separation as described above of the magnesium salt of *l*-isopulegyl hydrogen phthalate remains after the removal of the alcohol as a pasty mass, which is strongly dextrorotatory in ethyl-alcoholic solution. The mixture of hydrogen phthalates is recovered from the magnesium salts, has a specific rotatory power about  $\pm 0^\circ$ , and by careful fractional crystallisation from acetic acid can be further separated, the most soluble fraction having  $[\alpha]_{\text{D}}^{25}$  about  $+8^\circ$  in 5 per cent. ethyl-alcoholic solution. This dextrorotatory ester was dissolved in the calculated amount of a dilute solution of sodium carbonate and fractionally precipitated by small amounts of magnesium chloride solution. After repeating the process ten times,

the most soluble magnesium salt yielded a hydrogen phthalate which had  $[\alpha]_D + 30.1^\circ$  in ethyl alcohol ( $c=5$ ), and solidified in flat prisms melting at  $117^\circ$ . When hydrolysed, it yielded a dextro-rotatory  $\alpha$ -isopulegol (still containing, apparently, about 10 per cent. of *l*-isopulegol), which had  $D_{488}^{25} 0.9172$ ,  $[\alpha]_D^{25} + 29.3^\circ$ ,  $[\alpha]_{5461}^{25} + 34.5^\circ$ , and  $[\alpha]_{588}^{25} + 54.9^\circ$ .

When reduced by hydrogen in the presence of colloidal palladium, it gave an impure *d*-neomenthol with  $[\alpha]_{5461}^{25} + 10.9^\circ$ , which yielded a hydrogen succinate melting at  $68^\circ$  after two crystallisations from light petroleum, whereas the *l*-neomenthol described in Part II (*loc. cit.*) had  $[\alpha]_{5461}^{25} - 21.32^\circ$ , and gave a hydrogen succinate melting at  $67-68^\circ$ . The amount of material available did not permit of a further repetition of the exceedingly tedious process of separation. The isopulegones obtained from *l*-isopulegol, and the impure *d*- $\alpha$ -isopulegol by oxidation with chromic acid at  $50^\circ$  gave identical levorotatory oximes (m. p.  $121^\circ$ , and volatile in steam) and semicarbazones (m. p.  $171^\circ$ ).

#### *Esters of l-isopulegol and Normal Aliphatic Acids.*

The esters were prepared by the action of the requisite acid chlorides on a solution of isopulegol in pyridine, except in the case of the acetate, propionate, valerate, and heptate, where the acid anhydrides were employed. All are fragrant, limpid liquids at the ordinary temperature. Samples of isopulegol recovered from the esterification process, and also from the esters after these had undergone polarimetric examination, were unaltered in rotatory power. Two samples of isopulegyl valerate were also prepared by fractional esterification of the alcohol, and were identical in rotatory power.

In table II are given some of their physical properties, in table III the results of the determinations of their density ( $D_4^{25}$ ) and negative rotatory power ( $\alpha_{100}^{25}$ ), the second set of figures for the compounds being the resulting calculated values at the temperature named of the specific rotatory power, and in table IV the data of determinations of rotatory power in ethyl alcohol.

The densities were determined in a pycnometer holding about 1.5 c.c., except in the case of isopulegol, its acetate and propionate, when one holding 4 c.c. was used.

The rotations were measured in tubes of 50 mm. length, round which cooled water or heated mineral oil was circulated by means of a pump, but are here given as for 100 mm.

TABLE II.  
1-isoPulegol and its Esters.

	Boiling point °C./mm.	D <sub>20</sub> <sup>20</sup> .	n <sub>D</sub> <sup>20</sup> .	Molecular refractive power.*		Refractive dispersion n <sub>D</sub> <sup>20</sup> - n <sub>D</sub> <sup>15</sup> - n <sub>D</sub> <sup>10</sup> †
				$\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$ observed.	Difference from calculated value.	
1-isoPulegol .....	94°/14	0.9110 (at 20°)	1.4723 (at 20°)	47.41	+0.25	0.01464
Acetate .....	103°/14	0.9350	1.4565	57.08	0.52	0.01402
Propionate .....	91°/4	0.9300	1.4558	61.41	0.56	0.01397
n-Butyrate .....	116°/5	0.9245	1.4563	69.76	0.51	0.01381
n-Valerate .....	119°/4	0.9185	1.4576	75.73	0.58	0.01350
n-Hexate .....	153°/13	0.9113	1.4588	75.23	0.25	0.01343
n-Heptate .....	158°/15	0.9055	1.4584	79.83	0.27	0.01353
n-Octate .....	161°/6	0.9053	1.4601	84.42	0.26	0.01342
n-Nonylate .....	158°/2	0.9020	1.4603	89.04	0.27	0.01334
n-Decate .....	164°/2	0.8969	1.4614	93.65	0.28	0.01334
n-Undecate .....	188°/3	0.8969	1.4621	98.46	0.48	0.01329
n-Dodecate .....	189°/2	0.8933 (at 20°)	1.4618 (at 20°)	103.10	0.52	0.01331
Myristate .....			1.4618	112.10	0.31	0.01331

\* The structure of the isopropyl ring causes an increment of about 0.25 above the ordinary calculated value of the molecular refraction according to the Lorentz and Lorenz formula. It has often been observed (see Pickard and Kenyon, *loc. cit.*) that the members of homologous series containing five and eleven atoms in the growing chain have molecular refractions which differ from the calculated values by small amounts just greater than the experimental error.

† These values when plotted against molecular weight lie approximately on a continuous curve, becoming constant at about the ninth member of the series.

TABLE III.

*l*-iso*Pulegol*.

Temp. ....	18.4°	36.5°	70.5°	98.5°	131°	172°
D <sub>4</sub> .....	0.9123	0.8962	0.8661	0.8415	0.8134	0.7764
Temp. ....	15.5°	57.5°	105°	147°	163°	
$\alpha_{5438}^t$ .....	16.60	16.61	16.66	16.72	16.74	
Temp. ....	15.5°	56.5°	93.5°	141.5°	168°	
$\alpha_{5461}^t$ .....	23.60	23.74	23.70	23.82	23.98	
Temp. ....	15.5°	57°	101.5°	148°	165°	
$\alpha_{5086}^t$ .....	27.64	27.76	27.86	28.22	28.38	
Temp. ....	15.5°	56.5°	105.5°	150°	166.5°	
$\alpha_{4800}^t$ .....	31.46	31.78	32.36	32.80	32.98	
Temp. ....	15.5°	56.5°	103.5°	147°		
$\alpha_{4358}^t$ .....	39.20	39.86	40.52	41.38		
Temp. ....	20°	40°	60°	80°	100°	120° 140° 160°
$[a]_{5438}^t$ .....	18.23	18.61	18.98	19.39	19.83	20.26 20.73 21.22
$[a]_{5461}^t$ .....	25.90	26.46	27.05	27.65	28.28	28.95 29.66 30.38
$[a]_{5086}^t$ .....	30.31	31.01	31.74	32.47	33.25	34.08 34.95 35.83
$[a]_{5336}^t$ .....	34.51	35.43	36.37	37.35	38.37	39.45 40.57 41.74
$[a]_{4358}^t$ .....	43.07	44.30	45.55	46.86	48.22	49.67 51.16 52.71

*l*-iso*Pulegyl Acetate*.

Temp. ....	16.1°	41.4°	84.1°	131.9°	
D <sub>4</sub> .....	0.9364	0.9149	0.8794	0.8359	
Temp. ....	5.5°	21°	41°	66.5°	82°
$\alpha_{6138}^t$ .....	7.54	9.10	10.62	12.84	14.14
Temp. ....	0.5°	5.5°	21°	41°	64.5° 84°
$\alpha_{5461}^t$ .....	8.78	9.40	11.56	14.18	17.06 19.12
Temp. ....	5.5°	21°	41°	65°	81.5°
$\alpha_{5086}^t$ .....	10.16	12.92	15.90	19.40	21.54
Temp. ....	5.5°	21°	41°	65.5°	84.5°
$\alpha_{4800}^t$ .....	10.74	13.80	17.34	21.48	24.48
Temp. ....	0	5.5°	21°	41°	64.5° 83°
$\alpha_{4358}^t$ .....	9.48	10.98	14.82	19.70	24.70 28.56
Temp. ....	20°	40°	60°	80°	
$[a]_{5438}^t$ .....	9.58	11.61	13.65	15.82	
$[a]_{5461}^t$ .....	12.22	15.32	18.34	21.23	
$[a]_{5086}^t$ .....	13.61	17.18	20.74	24.16	
$[a]_{5336}^t$ .....	14.57	18.71	22.83	26.95	
$[a]_{4358}^t$ .....	15.65	21.24	26.38	31.66	

TABLE III. (*continued*).*l*-iso*Pulegyi* Propionate.

Temp. ....	12.2°	16.3°	44.6°	56.4°	82.6°	89.6°	131.3°
$D_4^t$ .....	0.9346	0.9315	0.9084	0.8987	0.8771	0.8721	0.8337
Temp. ....	3°	21.8°	46°	67°	84.5°		
$n_{D,20}^t$ .....	5.74	7.78	9.82	11.44	13.02		
Temp. ....	2°	21.8°	45°	67°	85°		
$n_{D,40}^t$ .....	6.80	9.64	13.08	15.58	17.88		
Temp. ....	2.5°	21.8°	46°	67°	84.5°		
$n_{D,60}^t$ .....	7.02	10.68	14.46	17.62	20.18		
Temp. ....	2°	21.8°	45.5°	67°	84.5°		
$n_{D,80}^t$ .....	7.20	11.14	15.80	19.38	22.50		
Temp. ....	2°	21.8°	45°	67.5°	85°		
$n_{D,100}^t$ .....	6.66	11.86	17.66	22.76	26.64		
Temp. ....	20°	40°	60°	80°			
$[a]_{D,20}^{25}$ .....	8.19	10.17	12.22	14.33			
$[a]_{D,40}^{25}$ .....	10.13	13.49	16.58	19.63			
$[a]_{D,60}^{25}$ .....	11.06	14.80	18.51	22.21			
$[a]_{D,80}^{25}$ .....	11.63	16.12	20.36	24.68			
$[a]_{D,100}^{25}$ .....	12.20	17.98	23.54	29.04			

*l*-iso*Pulegyi* *n*-Butyrate.

Temp. ....	20°	43.5°	54°	72°	113°	131°	147°
$D_4^t$ .....	0.9230	0.9046	0.8965	0.8822	0.8451	0.8293	0.8137
Temp. ....	3°	15°	34°	52°	71°	82°	108°
$n_{D,20}^t$ .....	3.20	4.50	6.46	8.08	9.70	10.76	12.76
Temp. ....	3°	15°	34°	55°	71.5°	86°	112°
$n_{D,40}^t$ .....	3.10	5.02	8.20	11.20	13.26	14.88	18.08
Temp. ....	3°	15°	34°	55°	75°	84°	109°
$n_{D,60}^t$ .....	2.90	5.60	8.82	12.28	15.36	16.66	20.50
Temp. ....	3°	15°	34°	54°	75°	86°	108°
$n_{D,80}^t$ .....	2.78	5.34	9.42	13.40	16.62	18.28	22.96
Temp. ....	3°	15°	34°	55°	72°	86°	110°
$n_{D,100}^t$ .....	1.00	4.32	9.52	14.98	18.84	22.04	27.12
Temp. ....	20°	40°	60°	80°	100°	120°	140°
$[a]_{D,20}^{25}$ .....	5.53	7.78	9.87	11.87	14.12	16.31	18.21
$[a]_{D,40}^{25}$ .....	6.16	9.99	13.32	16.24	19.39	22.40	25.54
$[a]_{D,60}^{25}$ .....	7.02	10.98	14.69	18.35	22.11	26.00	29.34
$[a]_{D,80}^{25}$ .....	6.93	11.77	16.13	19.88	24.65	28.77	32.96
$[a]_{D,100}^{25}$ .....	6.28	12.31	18.10	23.41	29.09	34.59	39.86



TABLE III. (continued).

## 1-isoPulegyll n-Valerate.

Temp. ....	22°	30°	56.5°	68.5°	75°	87°	127°
D <sub>4</sub> .....	0.9159	0.9095	0.8882	0.8787	0.8735	0.8630	0.8264
Temp. ....	2°	14.5°	16°	41°	51.5°	61°	87°
$n_{D_4}^{20}$ .....	3.74	5.24	5.36	7.64	8.54	9.20	11.06
Temp. ....	2°	15°	16°	41°	51°	60.5°	87°
$n_{D_4}^{25}$ .....	4.10	6.24	6.32	9.98	11.14	12.20	15.16
Temp. ....	2°	15°	16°	41°	51.5°	61°	87°
$n_{D_4}^{30}$ .....	4.26	6.78	6.88	10.90	12.54	13.80	17.20
Temp. ....	1.5°	15°	16°	41°	51°	60°	87°
$n_{D_4}^{40}$ .....	4.12	6.92	7.02	11.66	13.72	15.28	19.20
Temp. ....	0.5°	15°	16°	41°	51.5°	60°	87.5°
$n_{D_4}^{50}$ .....	3.02	6.66	6.78	12.92	15.38	17.14	22.32
Temp. ....	20°		40°		60°		80°
[ $n_D^{20}$ ] <sub>5435</sub> .....	6.28		8.39		10.32		12.19
[ $n_D^{20}$ ] <sub>5461</sub> .....	7.57		10.87		13.78		16.51
[ $n_D^{20}$ ] <sub>5086</sub> .....	8.28		11.99		15.47		18.79
[ $n_D^{20}$ ] <sub>5280</sub> .....	8.57		12.87		17.12		20.95
[ $n_D^{20}$ ] <sub>5358</sub> .....	8.63		14.16		19.36		24.11

## 1-isoPulegyll n-Hexanoate.

Temp. ....	14.6°	32.8°	42°	55.2°
D <sub>4</sub> .....	0.9187	0.9040	0.8972	0.8870
Temp. ....	6°	14.5°	40.5°	68°
$n_{D_4}^{20}$ .....	3.32	4.14	6.76	8.84
Temp. ....	6.5°	15°	41.5°	68°
$n_{D_4}^{25}$ .....	3.62	4.54	8.38	11.44
Temp. ....	6°	14.5°	41.5°	68°
$n_{D_4}^{30}$ .....	3.44	4.72	9.10	12.92
Temp. ....	6.5°	15°	41°	68°
$n_{D_4}^{40}$ .....	3.12	4.84	9.62	14.18
Temp. ....	6.5°	15°	42°	68°
$n_{D_4}^{50}$ .....	1.94	4.16	10.82	16.28
Temp. ....	20°	40°	60°	80°
[ $n_D^{20}$ ] <sub>5425</sub> .....	5.19	7.45	9.33	11.06
[ $n_D^{20}$ ] <sub>5461</sub> .....	5.95	9.04	11.93	14.86
[ $n_D^{20}$ ] <sub>5096</sub> .....	6.19	9.84	13.31	16.77
[ $n_D^{20}$ ] <sub>5090</sub> .....	6.30	10.46	14.55	18.41
[ $n_D^{20}$ ] <sub>5294</sub> .....	5.84	11.46	16.66	21.47

TABLE III. (*continued*).*l*-isoPulegyl *n*-Heptoate.

Temp. ....	18°	39.5°	80°	96°		
$D_4^{20}$ .....	0.9111	0.8948	0.8802	0.8522		
Temp. ....	5.5°	21.5°	33.5°	44°	66.5°	83°
$n_{D,20}^{25}$ .....	3.08	4.48	5.54	6.22	7.90	9.08
Temp. ....	6.5°	21.5°	33.5°	44°	66°	87°
$n_{D,20}^{25}$ .....	3.20	5.10	6.66	8.04	10.56	12.76
Temp. ....	5.5°	21.5°	34°	40°	65.5°	84°
$n_{D,20}^{25}$ .....	2.92	5.42	7.56	8.56	11.72	14.06
Temp. ....	6.5°	21.5°	34°	44°	66°	85°
$n_{D,20}^{25}$ .....	2.70	5.56	8.00	9.64	13.12	15.84
Temp. ....	7°	21.5°	33.5°	44°	65.5°	87°
$n_{D,20}^{25}$ .....	1.82	5.28	8.16	10.44	14.54	18.74
Temp. ....	20°		40°		60°	80°
$[\alpha]_{D,20}^{25}$ .....	4.84		6.71		8.43	10.17
$[\alpha]_{D,20}^{25}$ .....	5.48		8.45		11.27	13.88
$[\alpha]_{D,20}^{25}$ .....	5.76		9.44		12.57	15.68
$[\alpha]_{D,20}^{25}$ .....	5.83		10.07		13.82	17.53
$[\alpha]_{D,20}^{25}$ .....	5.50		10.74		15.41	20.09

*l*-isoPulegyl *n*-Octoate.

Temp. ....	19°		23°		38°		52.5°
$D_4^{20}$ .....	0.9055		0.9028		0.8925		0.8828
Temp. ....	3°	17.3°	42°	45°	62°	76.5°	82°
$n_{D,20}^{25}$ .....	2.40	3.90	6.06	6.24	7.32	8.28	8.56
Temp. ....	3.5°	17.3°	37°	42°	63°	68.5°	86.5°
$n_{D,20}^{25}$ .....	2.64	4.36	6.74	7.30	9.54	10.12	11.90
Temp. ....	3°		15°		41.5°		67.5°
$n_{D,20}^{25}$ .....	2.44		4.50		8.10		11.30
Temp. ....	3°	17.3°	41.5°		61°		67°
$n_{D,20}^{25}$ .....	2.00	4.78	8.86		11.76		12.56
Temp. ....	3.5°	17.3°	37°		43.5°		60°
$n_{D,20}^{25}$ .....	0.74	4.08	8.36		9.70		13.08
Temp. ....	20°		40°		60°		80°
$[\alpha]_{D,20}^{25}$ .....	4.60		6.58		8.28		9.78
$[\alpha]_{D,20}^{25}$ .....	5.23		7.92		10.52		13.09
$[\alpha]_{D,20}^{25}$ .....	5.68		8.84		11.88		14.84
$[\alpha]_{D,20}^{25}$ .....	5.86		9.68		13.23		16.69
$[\alpha]_{D,20}^{25}$ .....	5.26		10.10		14.82		19.07

TABLE III. (continued).

*l*-isoPulegyl n-Nonoate.

Temp. ....	19.3°	36°	57.4°	
D <sub>d</sub> .....	0.9042	0.8925	0.8768	
Temp. ....	4°	23.5°	49.5°	81.5°
$\alpha_{4438}^t$ .....	2.58	4.26	6.18	8.00
Temp. ....	4.5°	23.5°	47°	63°
$\alpha_{5161}^t$ .....	2.44	4.94	7.58	9.34
Temp. ....	4°	23°	49°	81.5°
$\alpha_{5086}^t$ .....	2.42	5.34	8.64	12.22
Temp. ....	4°	23.5°	48°	81.5°
$\alpha_{4800}^t$ .....	2.30	5.52	9.34	13.54
Temp. ....	4.5°	23.5°	46°	63°
$\alpha_{4816}^t$ .....	1.16	5.14	9.68	12.72
Temp. ....	20°	40°	60°	80°
$[\alpha]_{6438}^t$ .....	4.36	6.20	7.72	9.20
$[\alpha]_{5461}^t$ .....	4.98	7.64	10.24	12.57
$[\alpha]_{5086}^t$ .....	5.38	8.43	11.39	14.06
$[\alpha]_{4800}^t$ .....	5.51	9.22	12.64	15.62
$[\alpha]_{4585}^t$ .....	4.94	9.47	13.94	18.12

*l*-isoPulegyl n-Decoate.

Temp. ....	17°	45.5°	65°	84°
D <sub>d</sub> .....	0.9028	0.8821	0.8684	0.8545
Temp. ....	1°	14°	44°	60°
$\alpha_{6133}^t$ .....	2.50	3.32	5.46	6.44
Temp. ....	3°	14°	42°	59°
$\alpha_{6161}^t$ .....	2.30	3.70	6.90	8.32
Temp. ....	1°	14°	42°	59°
$\alpha_{5086}^t$ .....	1.90	3.80	7.46	9.61
Temp. ....	1°	14°	41°	58°
$\alpha_{4900}^t$ .....	1.96	3.90	7.88	10.38
Temp. ....	3°	14°	42°	58°
$\alpha_{4513}^t$ .....	0.58	3.38	8.94	11.48
Temp. ....	20°	40°	60°	80°
$[\alpha]_{6133}^t$ .....	4.15	5.78	7.41	9.02
$[\alpha]_{5161}^t$ .....	4.93	7.52	9.75	11.92
$[\alpha]_{5086}^t$ .....	5.20	8.19	11.10	13.69
$[\alpha]_{4800}^t$ .....	5.35	8.71	12.23	15.20
$[\alpha]_{4513}^t$ .....	5.15	9.66	13.54	17.38

TABLE III. (*continued*).*isoPulegyt n-Undecate.*

Temp. ....	17°	55°	88.5°	131°		
D <sub>4</sub> <sup>20</sup> .....	0.8972	0.8715	0.8475	0.8138		
Temp. ....	3.5°	15.5°	38.5°	56°	88°	
n <sub>D,138</sub> <sup>T</sup> .....	2.58	3.42	5.16	6.12	7.74	
Temp. ....	2°	15.5°	38.5°	56°	88.5°	
n <sub>D,131</sub> <sup>T</sup> .....	2.46	3.96	6.28	7.96	10.38	
Temp. ....	4°	15°	38.5°	55.5°	90°	
n <sub>D,138</sub> <sup>T</sup> .....	2.70	4.00	7.10	9.06	11.86	
Temp. ....	4.5°	15.5°	39°	55.5°	91°	
n <sub>D,130</sub> <sup>T</sup> .....	2.56	4.22	7.78	9.74	13.46	
Temp. ....	2.5°	15.5°	37.5°	53°	68.5°	87°
n <sub>D,138</sub> <sup>T</sup> .....	1.48	4.18	7.90	10.34	12.42	15.02
Temp. ....	20°	40°	60°	80°		
[α] <sub>D,138</sub> <sup>20</sup> .....	4.31	5.94	7.31	8.65		
[α] <sub>D,131</sub> <sup>20</sup> .....	4.98	7.35	9.48	11.48		
[α] <sub>D,126</sub> <sup>20</sup> .....	5.29	8.21	10.83	13.02		
[α] <sub>D,120</sub> <sup>20</sup> .....	5.54	8.94	11.82	14.52		
[α] <sub>D,115</sub> <sup>20</sup> .....	5.54	9.41	13.18	16.44		

*isoPulegyt n-Dodecate.*

Temp. ....	14°	20°	43°	58.5°	80°	
$D_4^{20}$ .....	0.8996	0.8959	0.8794	0.8684	0.8549	
Temp. ....	4°	17.5°	39°	56°	81°	
$n_{D,128}^T$ .....	2.44	3.30	4.64	5.78	7.14	
Temp. ....	4.5°	17°	40°	57°	80°	
$n_{D,125}^T$ .....	2.40	3.66	5.90	7.48	9.40	
Temp. ....	4°	18°	38°	55°	81°	
$n_{D,125}^T$ .....	2.36	4.10	6.46	8.34	10.70	
Temp. ....	4°	18°	38°	55°	81°	
$n_{D,120}^T$ .....	2.10	4.16	7.00	9.12	11.82	
Temp. ....	4.5°	17.5°	38°	53°	69.8°	82°
$n_{D,128}^T$ .....	1.44	3.52	7.26	9.58	12.08	13.90
Temp. ....	20°	40°	60°	80°		
$[a]_{D,128}^{20}$ .....	5.84	5.35	6.89	8.32		
$[a]_{D,121}^{20}$ .....	4.42	6.09	8.88	11.01		
$[a]_{D,115}^{20}$ .....	4.83	7.60	10.14	12.47		
$[a]_{D,110}^{20}$ .....	4.98	8.23	11.18	13.75		
$[a]_{D,105}^{20}$ .....	4.65	8.57	12.27	15.93		

TABLE III. (*continue.*).*l*-iso*Pulegyl Myristate*.

Temp. ....	12.4°	34.8°	54.8°	
D <sub>D</sub> <sup>20</sup> .....	0.8985	0.8832	0.8693	
Temp. ....	5°	22°	43°	65.5° 84.5°
n <sub>D</sub> <sup>5138</sup> .....	2.44	3.54	4.84	6.00 6.82
Temp. ....	5°	22°	43°	65° 83.5°
n <sub>D</sub> <sup>5161</sup> .....	2.40	3.96	5.86	7.62 9.10
Temp. ....	5°	22°	43°	65.5° 84°
n <sub>D</sub> <sup>5088</sup> .....	2.52	4.44	6.54	8.54 10.36
Temp. ....	5°	22°	43°	65.5° 83.5°
n <sub>D</sub> <sup>1800</sup> .....	2.42	4.58	7.08	9.26 11.44
Temp. ....	4.5°	22°	43°	65° 84°
n <sub>D</sub> <sup>1258</sup> .....	1.66	4.26	7.58	10.56 13.36
Temp. ....	20°	40°	60°	80°
[α] <sub>D</sub> <sup>435</sup> .....	3.81	5.30	6.63	7.82
[α] <sub>D</sub> <sup>461</sup> .....	4.23	6.30	8.32	10.33
[α] <sub>D</sub> <sup>506</sup> .....	4.68	7.05	9.38	11.69
[α] <sub>D</sub> <sup>480</sup> .....	4.84	7.62	10.28	13.00
[α] <sub>D</sub> <sup>483</sup> .....	4.48	8.07	11.44	15.02

Some of the materials used in this work were purchased from a grant made by the Government Committee of the Royal Society; the receipt of a personal grant from the Department of Scientific and Industrial Research to one of the authors is acknowledged, whilst the authors' thanks are also due to Messrs. Schimmel, of Leipzig, for a pre-war gift of crude *isopulegyl acetate*.

TABLE IV.  
*Determinations of Rotatory Power in (approx.) 5 per cent. Solution in Ethyl Alcohol.*

Ester.	Length of tube, Cm.	Weight of solute, Grams.	$\alpha_{440}^{\text{obs.}}$	$\alpha_{460}^{\text{obs.}}$	$\alpha_{480}^{\text{obs.}}$	$\alpha_{490}^{\text{obs.}}$	$[\alpha]_{440}^{\text{obs.}}$	$[\alpha]_{460}^{\text{obs.}}$	$[\alpha]_{480}^{\text{obs.}}$	$[\alpha]_{490}^{\text{obs.}}$	$[\alpha]_{490}^{\text{calc.}}$
<i>i</i> -isoPulegi Acetate .....	20	1.0020	1.67	2.07	2.46	2.66	16.66	20.66	23.95	26.55	29.44
Propionate .....	20	0.9926	1.57	1.95	2.27	2.49	15.81	19.64	22.87	25.08	27.70
<i>n</i> -Butyrate .....	20	1.0060	1.42	1.66	1.93	2.08	14.11	16.50	19.19	20.67	23.56
<i>n</i> -Valerate .....	20	0.9944	1.42	1.67	1.96	2.15	14.28	16.79	19.71	21.62	24.13
<i>n</i> -Hexoate .....	20	0.8353	0.95	1.20	1.43	1.57	11.37	14.36	17.12	18.79	21.07
<i>n</i> -Heptoate .....	20	0.9988	1.08	1.38	1.59	1.71	10.81	13.82	15.92	17.12	19.83
<i>n</i> -Octoate .....	20	0.9996	1.03	1.35	1.51	1.68	10.30	13.50	15.10	16.81	19.21
<i>n</i> -Nonoate .....	20	0.9990	1.02	1.36	1.48	1.63	10.21	13.01	14.81	16.31	18.72
<i>n</i> -Decoate .....	20	1.0030	0.98	1.25	1.42	1.57	9.77	12.47	14.16	15.65	17.55
<i>n</i> -Undecoate .....	20	0.9940	0.98	1.18	1.36	1.53	9.86	11.87	13.68	15.39	16.40
<i>n</i> -Dodecoate .....	20	1.0175	0.96	1.21	1.38	1.53	9.44	11.90	13.56	15.04	16.51
Myristate .....	20	0.9957	0.92	1.09	1.27	1.41	9.24	10.95	12.76	14.16	15.46

All solutions for the observations of rotatory power recorded above were prepared by making up about 1 gram of the substance to 20 c.c., with alcohol at 20°, at which temperature all observations were also made.

CXXXVI.—*Some New Azopyrazolones and Allied Compounds.*

By KENNETH HERBERT SAUNDERS.

IN seeking to ascertain the effect produced on the colour of compounds of the azo-type belonging to the benzene, naphthalene, and anthraquinone groups by increasing molecular weight by a comparison of the absorption spectra of the various members, it was found that scarcely any of the required substances beyond the benzeneazo- and naphthaleneazo-series have been prepared. Although azobenzene and the azonaphthalenes are very well known,  $\alpha$ -azoanthraquinone has only been discovered in recent years (Gattermann and Ebert, *Ber.*, 1916, **49**, 2117), whilst the azoanthracenes are unknown. For the purpose of such a comparison, the azopyrazolones, being more strongly coloured and more faster to light than the corresponding members of the azobenzene series, would seem to be more suitable, and have therefore been selected for the investigation. A complete series of compounds has been prepared in which the anthraquinone nucleus is introduced either into the 1-position of the pyrazolone ring or as the first component of an azopyrazolone compound, or in both positions together.

The 1-anthraquinonylpyrazolones cannot be obtained by the simple process of heating ethyl acetoacetate with the required hydrazine, because reaction invariably stops with the formation of the hydrazone. The further action of condensing agents is necessary before the  $\beta$ -anthraquinonylhydrazone of ethyl acetoacetate can be converted into a pyrazolone. Although boiling sulphuric acid will effect this change in one stage, the yield of the pyrazolone is small, a large proportion of the original hydrazine being regenerated. A far more satisfactory method is to boil the hydrazone with acetic anhydride, whereby 1- $\beta$ -anthraquinonyl-acetyl-3-methylpyrazolone is produced (Möhlau and Reiner, *Ber.* 1912, **45**, 2244), and then hydrolyse with hydrochloric acid. 1- $\beta$ -Anthraquinonyl-3-methyl-5-pyrazolone is obtained in this way as an orange powder showing all the properties of the class except that the anthraquinone nucleus causes it to be highly insoluble and rather slow to enter into reaction. It couples with diazonium salt in acetic acid solution to give typical arylazopyrazolones of great stability, which do not show definite melting points, but slowly begin to decompose above 250° or thereabout.

The sole product of the complete condensation of the  $\alpha$ -anthra-

quinonylhydrazone of ethyl acetoacetate is pyrazoleanthrone, and the required pyrazolone cannot be obtained (Reiner, *Diss.*, Dresden, 1912; Möhlau and Viertel, *Ber.*, 1912, **45**, 3238). Difficulty in obtaining the  $\alpha$ -isomeride is also experienced in the preparation of the 1-naphthyl-5-pyrazolones (Knorr, *Ber.*, 1884, **17**, 550), for whilst 1- $\beta$ -naphthyl-5-pyrazolone is easily produced, the product obtained from the fusion of  $\alpha$ -naphthylhydrazine with ethyl acetoacetate contains scarcely any pyrazolone, whilst in solvents the condensation does not take place at all. As noted above, the colour of  $\beta$ -anthraquinonylpyrazolone is orange, although all the other pyrazolones of this type hitherto described are colourless. The colour vibration may be set up by the carbonyl group of the pyrazolone reacting with that of the anthraquinone nucleus, owing to their being so arranged in space that they are in the closest proximity. That the colour is concerned with these two groups is shown by the fact that acetylation of the pyrazolone changes the colour to lemon-yellow. It seems possible, therefore, that the colour of the products, and also the difficulty of introducing the  $\alpha$ -anthraquinonyl group, may be referred to the contiguous position of the carbonyl groups in the anthraquinone and pyrazolone nuclei. Evidence for this view would be the preparation of the 1- $\alpha$ -naphthyl- and 1- $\alpha$ -anthraquinonyl-3-pyrazolone, but these compounds do not yet seem to have been described.

For the preparation of the arylazo-derivatives of the above anthraquinonylpyrazolone, the alternative process, due to Bülow and Hecking (*Ber.*, 1911, **44**, 437), has also been investigated. The first two steps are easily accomplished,  $\beta$ -anthraquinone-diazonium sulphate, for example, readily combining with ethyl acetoacetate, whilst the azo-compound so formed, on boiling with hydroxylamine, passes into the *isooxazalone*. When, however, the *isooxazalone* is treated with hydrazines, although a yield approaching theoretical is obtained from hydrazine itself, the yield steadily falls as phenyl, naphthyl, and anthraquinonyl nuclei are introduced, so that the method is useless for producing the higher members of the series.

Sodium dihydroxytartrate decomposes below a temperature at which  $\beta$ -anthraquinonylhydrazine will react, excepting with extreme slowness, so that it was found impossible to obtain new members of the tartrazine group by this method, all products of reaction from a large variety of solvents being for the most part a mixture of the decomposition products of the dihydroxytartrate.

The anthraquinoneazopyrazolones, whether unsubstituted in the 1-position or substituted by phenyl, naphthyl, or anthraquinonyl residues, are characterised by having, at best, only a sparing solu-



bility in most organic solvents. They can be crystallised fairly well from pyridine or nitrobenzene. They also have the property of many anthraquinoneazo-compounds of dissolving in warm alkali hydroxide to form a deep purple solution, and, in the case of 4- $\beta$ -anthraquinoneazo-3-methyl-5-pyrazolone, which is very readily soluble in this reagent, a monosodium salt can be crystallised by salting the warm solution. Their melting points are very high, so that often decomposition sets in before fusion takes place.

The property which first attracted attention to the group is that 4- $\beta$ -anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone can exist in two differently coloured modifications: (1) yellow, unstable, and (2) red, stable (Möhlau and Reiner, *Ber.*, 1912, **45**, 2240). These authors prepared both forms, and found that the same absorption spectrum is given by both, and that, on heating, the yellow form changes into the red without melting. The same behaviour is shown by 4- $\beta$ -anthraquinoneazo-1- $\beta$ -naphthyl-3-methyl-5-pyrazolone, excepting that the yellow form is still less stable, and only appears directly after combination has taken place, rapidly changing to the red form on warming. On the other hand, 4- $\beta$ -anthraquinoneazo-3-methyl-5-pyrazolone and 4- $\beta$ -anthraquinoneazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone exist in the solid state only in yellow forms, and by no means can be induced to crystallise otherwise. It would appear, therefore, that a phenyl, and more particularly a naphthyl, nucleus substituting the 1-position of the pyrazolone ring causes the ordinary yellow form to be unstable, with the result that slight rearrangement takes place on crystallisation, a more stable, red form being produced.

The colour of the solutions of the anthraquinoneazopyrazolones is deep yellow, almost indistinguishable to the eye from those of the benzeneazopyrazolones, the azo-compounds derived from 1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone, notwithstanding the red colour of this compound, showing practically the same colour as those in which the anthraquinone nucleus is absent from the 1-position of the pyrazolone ring. This agrees well with Hewitt's theory (*T.*, 1907, **91**, 1251), since the two carbonyl groups in the anthraquinone nucleus cut short the chain of double and single bonds, isolating the benzene ring beyond, so that it cannot add its effect, and thus the net result on the colour of an anthraquinone group in an azo compound of this type is practically that of a single benzene ring.

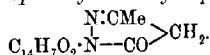
#### EXPERIMENTAL.

*$\beta$ -Anthraquinonoglydrazine.* For the purpose of this research, considerable quantity of this hydrazine was required. The

synthesis has been described in detail by Möhlau, Viertel, and Reiner in a comprehensive paper (*Ber.*, 1912, **45**, 2233), and also by Möhlau (*ibid.*, p. 2244). The latter paper deals with the preparation from  $\beta$ -chloroanthraquinone by heating with hydrazine hydrate, but as the yields are only about 20 per cent., the process is useless on the large scale. The former paper is an account of the process outlined in D.R.-P. 163447, consisting in the reduction of  $\beta$ -anthraquinonediazonium sulphate in aqueous solution with potassium hydrogen sulphite, followed by hydrolysis of the hydrazinedisulphonic acid with hydrochloric acid. Owing to the fact that all the intermediate compounds have to be isolated in the solid state, the process is lengthy and cumbersome, on account of the rather large volume of water necessary for the sparingly soluble  $\beta$ -anthraquinonediazonium sulphate. The reduction of the diazonium chloride with stannous chloride has therefore been tried.

If  $\beta$ -aminoanthraquinone is boiled with excess of concentrated hydrochloric acid until completely converted to the hydrochloride, it can be diazotised at the ordinary temperature as readily as in concentrated sulphuric acid. Completion is shown when a drop of the liquid diluted with water gives yellow diazonium sulphate, soluble on shaking, instead of aminoanthraquinone in red flakes.

The action of stannous chloride on such a solution is complex and leads to poor yields of  $\beta$ -anthraquinonylhydrazine. Even when strongly cooled with ice and salt, nitrogen is evolved during the reaction, and the total nitrogen content of the final product never rises above 7.5 per cent. This seems to be due to a two-fold cause. First, the anthraquinone-carbonyl groups are more easily reduced than the diazo-group, and, secondly, steric hindrance causes the general sluggishness of the  $\alpha$ -hydrogen in the hydrazine, reducing agents not being able to add this hydrogen, thus causing fission of the diazonium chloride to take place instead. It was further found that the addition of one molecule of stannic chloride caused the reaction to proceed more smoothly, a green, intermediate product being formed, but on isolating the free base it gave no better results on analysis. The hydrazone prepared from this hydrazine was purified only with difficulty, and, finally, the bulk of the hydrazine was prepared by the use of potassium salts, which give better yields and more uniform results than those of sodium, a constant yield of 70 per cent. being obtained.

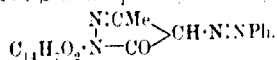
1- $\beta$ -Anthraquinonyl-3-methyl-5-pyrazolone,

$\beta$ -Anthraquinonylhydrazine was condensed with ethyl acetate in amyl alcohol solution, and the hydrazone recrystallised from alcohol. Ten grams of this boiled with 100 c.c. of acetic anhydride gave 7.5 grams of the acetylpyrazolone, which was dissolved in a mixture of 200 c.c. of glacial acetic acid and 75 c.c. of hydrochloric acid, and hydrolysed by two hours' boiling, latterly with the addition of animal charcoal. The mixture was cooled, filtered, and poured into excess of water, when 1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone separated as a yellowish-red, gelatinous mass, which was washed many times with cold water, and dried at 100°. The yield was 6.5 grams.

The pyrazolone is soluble in glacial acetic acid to an orange solution, which deposits minute, red crystals on cooling, more readily so in pyridine, but only sparingly so in alcohol and most other organic solvents; insoluble in water, dilute acids, or alkalis, but giving a red solution in concentrated sulphuric acid and a portwine coloured vat in alkaline hyposulphite.

It was recrystallised from pyridine, giving an orange powder, but although many combustions were carried out, neither satisfactory nor concordant results were obtained. This would seem to be due to the impossibility of effecting complete combustion, the nitrogen continuing to be evolved for long periods even at a bright red heat. The same trouble occurred to a less degree with the azo-derivatives, heating having to be continued for an unusual time before nitrogen ceased to be evolved.

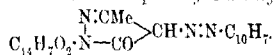
The following reactions, characteristic of the pyrazolones, were shown. In acetic acid solution the compound readily reacts with nitrous acid to give a sparingly soluble, pale yellow isonitroso-compound. Bromine water added to the same solution is at once decolorised, and a yellow precipitate of the dibromopyrazolone is formed. So far, a definite member of the antipyrine group has not been obtained.

1-Benzotriazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone,

To a solution of the pyrazolone in glacial acetic acid, the requisite quantity of benzenediazonium chloride was added. In the presence of sodium acetate, combination at once took place, a

yellow, gelatinous mass separating. After stirring for an hour at  $0^{\circ}$ , it was poured into water, collected, washed, and dried. It crystallises from pyridine, in which it is very readily soluble, in minute, yellow needles. It is soluble in nitrobenzene and, to a smaller extent, in glacial acetic acid; in concentrated sulphuric acid it gives a deep orange solution (Found: N=13.58.  $C_{14}H_{16}O_2N_4$  requires N=13.71 per cent.).

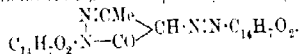
4- $\alpha$ -Naphthaleneazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone and  
4- $\beta$ -Naphthaleneazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone,



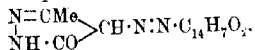
These were prepared in exactly the same way as the benzeneazo-compound. The former was obtained in minute, vermilion needles on crystallisation from pyridine, in which it is very sparingly soluble (about 0.75 gram in 100 c.c.). It gives a purple solution in concentrated sulphuric acid, whereas the  $\beta$ -naphthaleneazo-compound is deep orange in this solvent, the usual test which serves to distinguish the two isomerides, no matter what the 1-substituent of the pyrazolone ring is (Found: N=12.06.  $C_{24}H_{18}O_2N_4$  requires N=12.22 per cent.).

The second compound, being almost insoluble in pyridine, was crystallised from nitrobenzene, giving a dull red powder. Both are insoluble in most organic solvents (Found: N=12.10.  $C_{24}H_{18}O_2N_4$  requires N=12.22 per cent.).

4- $\beta$ -Anthraquinoneazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone,



$\beta$ -Aminoanthraquinone (1.1 grams), after conversion to the hydrochloride, was diazotised in 30 c.c. of glacial acetic acid with 30 per cent. excess of amyl nitrite (Kautler, *Zeitsch. Farben-Ind.*, 1903, **2**, 469). This was combined with 1.5 grams of the pyrazolone in acetic acid solution, giving a theoretical yield of the crude azo-compound. When crystallised from nitrobenzene, it forms fine, microscopic, yellow needles; variation of the conditions failed to produce any other form. It is insoluble in all solvents except nitrobenzene, and, to a less extent, in pyridine (Found: N=10.26.  $C_{22}H_{16}O_4N_4$  requires N=10.39 per cent.).

4  $\beta$ -Anthraquinoneazo-3-methyl-5-pyrazolone,

$\beta$ -Aminoanthraquinone (2.5 grams) was dissolved in 19 c.c. of sulphuric acid (D 1.84) with mechanical stirring. The beaker was surrounded with a water-jacket, and 4.5 grams of dry, crushed ice were added to the solution. In five minutes, a voluminous, white paste of  $\beta$ -aminoanthraquinone sulphate was formed. A solution of 1 gram of sodium nitrite was then added from a tap funnel with a very fine nozzle, so that an hour elapsed before all had been run in, whilst the temperature of the acid and the surrounding bath was allowed to rise to  $30^\circ$  under the heat of dilution. As the diazotisation proceeded, the  $\beta$ -aminoanthraquinone sulphate dissolved, and, on completion, a clear, brown solution resulted, a drop of which, added to water, gave a yellow precipitate, dissolving to a very pale yellow solution on shaking. Sufficient ice to dilute the warm solution enough to start the crystallisation of the  $\beta$ -anthraquinonediazonium sulphate was added, and the whole set aside to cool. In half an hour the diazonium salt crystallised in shining, yellow plates, the contents of the beaker setting solid. The mass was scraped out on to crushed ice, collected, and washed once with ice-water. The  $\beta$ -anthraquinonediazonium sulphate was obtained in this way as a yellow, stable, crystalline powder in a yield of 87 per cent. of the theoretical. It was dissolved by stirring into 100 c.c. of water at  $20^\circ$  and decomposed with a solution of 5 grams of sodium acetate.

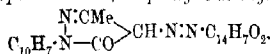
Ten grams of 3-methyl-5-pyrazolone having been dissolved in 250 c.c. of water, the diazo solution was added with stirring, and immediately the azo compound separated in yellow flakes. It was collected, washed twice with hot water, and dried at  $100^\circ$ ; the yield was theoretical.

This compound was found to be characterised by extreme insolubility in all organic solvents. It was crystallised from pyridine, in which it dissolved to the extent of less than 1 per cent., the crystals forming microscopic needles. It was also sparingly soluble in nitrobenzene or amyl alcohol; in concentrated sulphuric acid, the solution was orange (Found: N 17.12.  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_4$  requires N = 16.90 per cent.).

When warmed with dilute sodium hydroxide solution, it dissolved readily, giving a deep purple solution. On salting the hot solution, shining, purplish-black crystals were deposited, and on acidifying a solution of these, the original azopyrazolone was precipitated as a yellow jelly. By titration of a solution with 0.1N

hydrochloric acid, using the above colour change as indicator, it was found that the salt contained one atom of sodium.

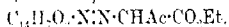
*4-β-Anthraquinoneazo-1-β-naphthyl-3-methyl-5-pyrazolone,*



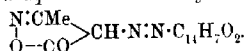
Four grams of 1-β-naphthyl-3-methyl-5-pyrazolone dissolved inacial acetic acid were combined with the anthraquinonediazonium sulphate, prepared from 4.6 grams of β-aminoanthraquinone diazotised as above. The azo-compound, obtained as a flocculent, range mass on dilution with water, was collected, washed twice with cold water and once with hot, and dried at 100°. It gave brick-red needles when crystallised from nitrobenzene, in which it is fairly soluble at the boiling point. Crystallisation of the cool solution diluted with alcohol, conditions under which 4-β-anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone gives a large proportion of the yellow form, failed to give any other variety. It is also soluble in pyridine or glacial acetic acid, whilst in alcoholic sodium hydroxide it gives the typical purple solution; in concentrated sulphuric acid its solution is deep red (Found: N=12.46.  $\text{C}_{24}\text{H}_{15}\text{O}_3\text{N}_4$  requires N=12.25 per cent.).

Attempts were made to prepare the isomeric 4-β-anthraquinone-azo-1-α-naphthyl-3-methyl-5-pyrazolone, but the results were unsatisfactory, and a pure substance was not obtained.

*Ethyl β-Anthraquinoneazoacetate,*



The β-anthraquinonediazonium sulphate resulting from the diazotisation of 10 grams of β-aminoanthraquinone was dissolved in a litre of water to which were added 20 grams of sodium acetate. To this, a solution of 5.1 grams of ethyl acetoacetate dissolved in 30 c.c. of N-sodium hydroxide was added, and the whole stirred until the odour of the ester had disappeared. The yellow azo-compound, being quite insoluble in water, separated at once, and was collected, washed, and dried. The yield was theoretical, calculating from the anthraquinonediazonium sulphate used. The crude substance had a green tinge, but, after boiling with animal charcoal and recrystallising from glacial acetic acid, it gave a yellow powder melting at 216–218°. It is surprisingly soluble for an anthraquinone derivative, dissolving in alcohol, chloroform, benzene, toluene, nitrobenzene, or pyridine. Alkali hydroxide turns it purple, but it is sparingly soluble, and acids precipitate it as a yellow jelly (Found: N=7.81.  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2$  requires N=7.69 per cent.).

4- $\beta$ -Anthraquinoneazo-3-methylisooxazalone,

Eight grams of ethyl  $\beta$ -anthraquinoneazoacetate were dissolved in a mixture of 175 c.c. of glacial acetic acid and 25 c.c. of an aqueous solution of 3 grams of sodium acetate. To the warm solution, 1.5 grams of hydroxylamine hydrochloride, dissolved in 10 c.c. of water, were added, and the whole was boiled for two hours, when a drop no longer showed a reducing action on Fehling's solution. The colour was then orange. Animal charcoal was added, and the whole boiled for a further ten minutes, filtered hot through asbestos, and slowly cooled. A mass of orange, needle-shaped crystals was deposited, and these were collected and dried; the yield was 6 grams. The substance melted and decomposed at 188–191°. It was soluble in acetic acid, alcohol, chloroform, benzene, or toluene, insoluble in water or dilute mineral acids, and sparingly soluble to a purple solution in alkali hydroxide (Found: N=12.01.  $\text{C}_{19}\text{H}_{15}\text{O}_4\text{N}_3$  requires N=12.68 per cent.).

On treating an acetic acid solution of the isooxazalone with hydrazine, so voluminous a precipitate of 4- $\beta$ -anthraquinoneazo-3-methyl-5-pyrazolone was obtained that the whole set solid. This substance was identified by the properties given above. With phenylhydrazine, a small crop of 4- $\beta$ -anthraquinoneazo-1-phenyl-3-methyl-5-pyrazolone was obtained and identified by its melting point. With the naphthylhydrazines, the products were too impure and tarry to identify with certainty. When 1 gram was boiled with 0.9 gram of  $\beta$ -anthraquinonylhydrazine, a precipitate of 0.8 gram of a red substance was obtained. By its insolubility in all solvents, except nitrobenzene, and its giving a reddish-purple solution in alkaline hyposulphite, it was concluded that it was 4- $\beta$ -anthraquinoneazo-1- $\beta$ -anthraquinonyl-3-methyl-5-pyrazolone, but the yield being so poor and the product so impure, this method of preparation was abandoned, as being too wasteful of the valuable  $\beta$ -anthraquinonylhydrazine.

The author wishes to express his thanks to the Salter's Institute of Industrial Chemistry for a Fellowship which enabled the work to be conducted, to Sir William Pope for his inspiration and interest, and to Dr. M. O. Forster for his guidance throughout the course of the work.

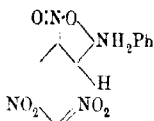
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[Received, September 18th, 1920.]

CXXXVII.—*The Action of Amines on Trinitrophenylmethylnitroamine.*

By THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and  
ROBERT ILLTYD LEWIS.

It is a well-known property of polynitro-aromatic compounds that they form additive derivatives with various types of aromatic substances, such as hydrocarbons, phenols, amines, etc. The most recent work on these derivatives has been carried out by Sudborough and his collaborators, who have examined in detail the formation and properties of a large series of the additive compounds formed by *s*-trinitrobenzene. In a review of the compounds prepared by them, Sudborough and Beard (T., 1910, **97**, 773) were led to suggest a possible formula for the compound of trinitrobenzene with aniline, representing it as possessing a hemi-quinonoid structure:



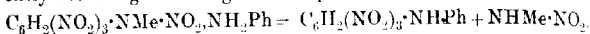
The present investigation was undertaken with a view to ascertain whether trinitrophenylmethylnitroamine (tetryl) forms additive compounds of a similar type to *s*-trinitrobenzene. It was observed that solutions of this substance in a variety of solvents became deeply coloured on the addition of any amine, primary, secondary, or tertiary, except in such cases where the amine contains strongly negative radicles, and in a large number of cases it has been possible to isolate from these solutions definite crystalline compounds, which are, without exception, compounds of tetryl and the base, united in equimolecular proportions. Owing to the fact that the additive compounds are largely dissociated in solution, the separation of the pure product is difficult in cases where the constituents are less readily soluble than the additive product.

The general conclusions drawn by Sudborough and Beard (*loc. cit.*) regarding stability and depth of colour have been confirmed, although the stability of this series of compounds is, on the whole, less than that of the corresponding compounds of the trinitrobenzene series. Thus, additive compounds of tetryl with phenols and tertiary amines have not been isolated in a pure state, although evidence of their formation is afforded by the production of a red colour when solutions of the components are mixed, and also, in



some cases, by an investigation of the melting points of mixtures of the components. Hydrocarbons and nitrophenols do not yield additive products.

The chief point of difference between the additive compounds under consideration and those of the trinitrobenzene series is that, in many cases, like the additive compounds of picryl chloride with bases, described by Sudborough and Picton (T., 1906, **89**, 583), they readily undergo a change to a condensed compound; thus, the compound of trinitrophenylmethylnitroamine and aniline, on storing in a sealed tube or on slow crystallisation from a hot solvent, yields 2:4:6-trinitrodiphenylamine, condensation apparently occurring according to the equation



We have not succeeded in isolating the methylnitroamine, despite various attempts, and it is probably decomposed during the condensation. The products are identical with those formed by the action of picryl chloride on the amine, and in a number of cases exist in two or more modifications differing in crystalline form and colour (compare Sudborough and Picton, *loc. cit.*; Busch and Pungs, *J. pr. Chem.*, 1909, [ii], **79**, 545; Hantzsch, *Ber.*, 1910, **43**, 1678). It is of interest to note, however, that the first product is generally of a red colour, whilst yellow or orange modifications are obtained by the use of picryl chloride, this being due to the presence of hydrogen chloride, which is instrumental in converting red forms into yellow.

Molecular-weight determinations of the additive compounds indicate that, notwithstanding the development of deep colour in the solutions, dissociation into the components is almost complete in dilute solution.

#### EXPERIMENTAL.

The method of work consisted, in general, in allowing a cold saturated solution of tetryl in alcohol, acetone, or benzene, and treated with rather more than one molecular proportion of the amine in the same solvent or in ether, to remain until crystallisation took place. In many cases, crystals of the additive compound were deposited with ease; in others, condensation took place, and the picryl derivative was obtained as first product. When the mixed solutions were heated for some time on a water-bath or when the crystallisation was prolonged by leaving the solvent to evaporate slowly on a hot plate, the condensation compound was usually deposited.

*Ammonia.*—The addition of an alcoholic solution of ammonia (one and two equivalents, respectively, were used in different

experiments) to a saturated alcoholic solution of tetryl yielded a deep red solution of an additive compound, which it was not possible to isolate. The deep colour gradually disappeared on warming, and from the resulting yellow solution, picramide (m. p.  $188^{\circ}$ ), in a yield corresponding with 53 per cent. of the theoretical, crystallised out. The filtrate, on evaporation, provided a further yield of crystals, which proved to be ammonium picrate.

When dry ammonia was passed into a solution of tetryl in benzene, little action took place, but on the addition of a small amount of acetone, a deep red solution was produced, from which a fluorescent, green oil separated. This solidified, on keeping, to a deep green mass, which, when freshly prepared, had a strong odour of ammonia. It is soluble in water or alcohol, giving orange-coloured solutions, but it has not been obtained in good crystalline form, and the melting point is indefinite, the substance decomposing explosively on heating above  $100^{\circ}$ . After excess of ammonia is removed, the substance contains C=34.19, H=3.61, and N=24.97 per cent., corresponding with the formula  $C_{10}H_{12}O_8N_6$ .

*Methylamine.*—When treated with an alcoholic solution of methylamine, tetryl gives a deep red-coloured solution, which, after slight warming, deposits reddish-brown needles (m. p.  $112^{\circ}$ ) consisting of 2:4:6-trinitromethylamine (Romburgh, *Rec. trav. chim.*, 1883, **2**, 105). On recrystallising from alcohol containing a small proportion of acid, pure, yellow needles melting at  $114.8^{\circ}$  are obtained (Found: N=23.45. Calc.: N=23.09 per cent.).

*Benzylamine.*—This yields 2:4:6-trinitrophenylbenzylamine, consisting of chocolate-coloured needles (m. p.  $143.3^{\circ}$ ), which, when crystallised from alcohol containing a little acid, becomes golden-yellow and melts at  $144.8^{\circ}$  (Found: N=17.70.  $C_{13}H_{10}O_8N_4$  requires N=17.61 per cent.).

*Aniline.*—The additive compound of tetryl with aniline was readily obtained from benzene solution, and forms orange-red plates melting at  $64^{\circ}$  (Found: N=21.35.  $C_{13}H_{12}O_8N_4$  requires N=22.11 per cent.).

The substance decomposes on keeping in the air, by treatment with acids, and by treatment with many solvents, regenerating tetryl (0.5425 treated with acid gave 0.4064 tetryl, =74.91. Calc.: tetryl=75.48 per cent.).

On keeping in a sealed tube for several weeks, the substance became moist, and the product on crystallisation proved to be 2:4:6-trinitrodiphenylamine. This substance is also obtained by slow crystallisation of the original mixture from warm benzene, acetone, or alcohol solutions. It forms orange crystals melting at

178°, corresponding with the description of Bamberger and Muller (*Ber.*, 1900, **33**, 188).

*o-Toluidine*.—An additive compound with tetryl is readily obtained by adding a slight excess of the base to a hot solution of tetryl in benzene solution, and allowing to crystallise. It consists of brick-red crystals melting at 63° (Found: N=21.18; tetryl=72.7.  $C_{14}H_{14}O_8N_6$  requires N=21.32; tetryl=72.8 per cent.).

The substance decomposes on exposure to the atmosphere and also on recrystallisation, yielding tetryl. It does not, however, yield a condensation product, and 2:4:6-trinitrophenyl-*o*-tolylamine is not formed, even when the mixture of components is boiled for forty-eight hours in a reflux apparatus using various solvents.

*m-Toluidine*. The additive compound in this case has not been obtained in a pure form, as it is rapidly changed, even at the ordinary temperature, to a condensed derivative. The product obtained from a mixture of the components in benzene solution consists of deep red needles melting at about 80°, which on treatment with acid regenerate tetryl. On warming this product with benzene or with a mixture of chloroform and light petroleum and allowing to crystallise, bright scarlet needles are deposited which melt at 118.5° (Found: N=17.37.  $C_{13}H_{10}O_6N_4$  requires N=17.53 per cent.).

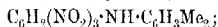
This substance, when first prepared, could be recrystallised from alcohol without change, but on the addition of a drop of acid to a saturated solution in alcohol, orange-yellow, prismatic crystals separated. These melt at 129° and correspond with 2:4:6-trinitrophenyl-*m*-tolylamine, as described by Busch and Pungs (*J. pr. Chem.*, 1909, [ii], **79**, 550). These authors state that the substance occurs in two forms, an orange modification (m. p. 129.5°) and a pure yellow form (m. p. 130°). The forms obtained by us are readily soluble in alkali hydroxide, yielding deep red solutions which, on acidifying, yield a pure yellow form melting at 129°. We have been unable, so far, to reconvert the stable yellow form into the labile scarlet form melting at 118.5°.

*p-Toluidine*. In the case of this amine, an additive compound with trinitrophenylmethylnitroamine is readily obtained by crystallising a mixture of the components from benzene or alcohol. It consists of deep red needles melting at 54°, which are readily decomposed by acids, regenerating tetryl (Found: N=20.82; tetryl=72.1.  $C_{11}H_{11}O_8N_6$  requires N=21.32; tetryl=72.8 per cent.).

The condensation compound, 2:4:6-trinitrophenyl-*p*-tolylamine, was obtained in the manner described above, and was isolated in

the two forms described by Busch and Pungs (*loc. cit.*, p. 548) as orange-yellow needles (m. p. 163–164°) and blood-red prisms (m. p. 165°).

*m-Xylidine*.—This base yields with tetryl a very unstable additive compound, which undergoes condensation very readily to form 2:4:6-trinitrophenyl-*m*-xylylamine,



this crystallises in orange-yellow needles melting at 157° (Found: N=17.11.  $\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_4$  requires N=16.86 per cent.).

*o-Anisidine*.—We were unable to isolate an additive compound in this case, although the colour of the solution indicated that such a compound is formed. From a warm solution in alcohol, red crystals of 2':4':6'-trinitro-2-methoxydiphenylamine separated, melting at 143° (Busch and Pungs, *loc. cit.*, p. 552, give 142°).

*p-Anisidine*.—In this case, again, no additive compound was isolated, for 2':4':6'-trinitro-4-methoxydiphenylamine was obtained even when cold solutions of the components were mixed. This consists of orange-red needles melting at 172.5° (Found: N=16.75. Calc.: N=16.77 per cent.).

Busch and Pungs (*loc. cit.*, p. 552) describe this compound as melting at 138°. We have repeated their preparation of the substance from picryl chloride and *p*-anisidine, and find that the product melts at 172.5°, as given above.

*p-Aminophenol*. The additive compound in this case has not been obtained pure, and readily passes into the condensed derivative, 2':4':6'-trinitro-4-hydroxydiphenylamine, which consists of brick-red needles melting at 171° (Turpin, T., 1891, **59**, 718).

*$\alpha$ -Naphthylamine*. The additive compound of this base is readily obtained by crystallising a mixture of the components in equivalent amounts from benzene. It consists of well-defined black prisms melting at 94°. The compound is of considerably greater stability than the additive compounds previously described, but is partly decomposed by crystallisation from many solvents, and completely by warming with acids (Found: N=19.73; tetryl=66.46.  $\text{C}_{17}\text{H}_{11}\text{O}_6\text{N}_4$  requires N=19.53; tetryl=66.73 per cent.).

No condensation product is formed, even after prolonged boiling of the additive compound or of a mixture of the components in a variety of solvents.

*$\beta$ -Naphthylamine*. The additive compound is similar to the above, and is obtained in black prisms melting at 90° (Found: N=19.72.  $\text{C}_{17}\text{H}_{11}\text{O}_6\text{N}_4$  requires N=19.53 per cent.).

The compound is fairly stable and does not yield a condensed derivative.

*m*-Phenylenediamine.—The additive compound of this base is readily obtained by crystallisation from benzene solution, and consists of silky, brown needles melting at  $84^{\circ}$ , which are moderately stable, but are partly decomposed by recrystallisation and completely by warming with acids (Found: N=24.94.  $C_{13}H_{13}O_3N_7$  requires N=24.81 per cent.).

The condensation compound, 2:4:6-trinitro-*m*-aminodiphenylamine, is obtained by slow crystallisation from hot acetone, and forms a deep red, crystalline powder melting at  $207^{\circ}$  (compare Jaubert, *Ber.*, 1898, **31**, 1182).

*Methylaniline*.—This base yields an additive compound with trinitrophenylmethylnitroamine, which consists of deep red plates melting at  $86^{\circ}$  (Found: N=21.86.  $C_{11}H_{11}O_3N_6$  requires N=21.32 per cent.).

The condensation compound has not been obtained by our general method.

Dimethylaniline, ethylaniline, and diethylaniline all yield deeply coloured solutions when mixed with solutions of tetryl, but pure additive compounds have not yet been obtained in these cases. Moreover, condensation to picryl derivatives does not occur even after prolonged boiling in alcohol or acetone solutions.

Similarly, *m*-nitroaniline and *p*-nitroaniline yield slightly coloured solutions with tetryl, but the separation of pure additive compounds has not been achieved. An investigation of the freezing-point curves of mixtures of these bases with tetryl indicates that unstable molecular compounds can exist.

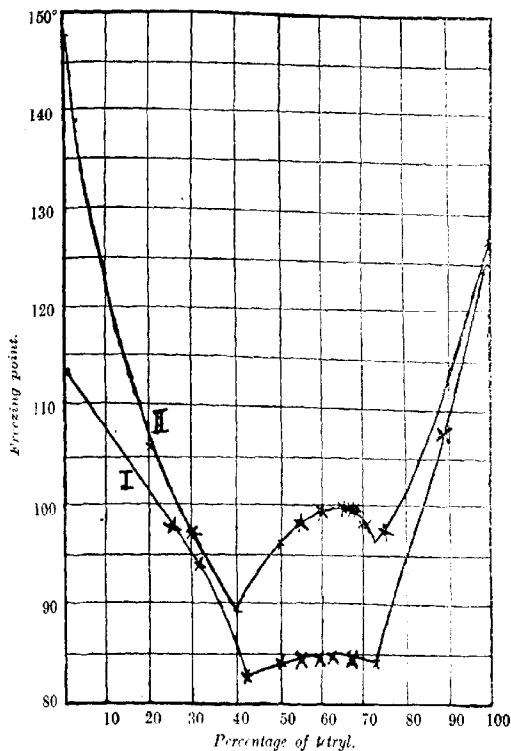
Halogen-substituted amines give only feeble colorations with solutions of tetryl, and form no additive compounds; condensation is also not possible.

#### *Summary and Conclusion.*

Trinitrophenylmethylnitroamine (tetryl) readily forms equimolecular additive compounds with the simpler amines, which in many cases readily condense to form picrylamines. The presence of alkyl substituents in the ortho position in the amine does not affect the formation of the additive compound, but inhibits the condensation. The presence of the methoxy-group in the ortho position does not, however, prevent the condensation (compare *o*-toluidine and *o*-anisidine). On the other hand, substitution in the meta-position renders the molecular compound unstable, and it readily passes into the corresponding picrylamine. The naphthylamines and the secondary amines yield stable additive

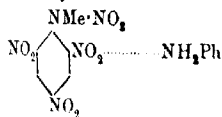
compounds, which do not pass into condensation derivatives (compare Sudborough and Picton, *loc. cit.*, p. 589).

According to Werner, the components of molecular compounds

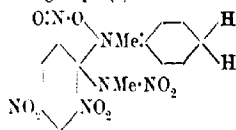


Freezing point curves of tetryl-*m*-nitroaniline (I) and tetryl-*p*-nitroaniline mixtures (II).

of this type are to be represented as united by the residual or auxiliary valencies of the nitro- and amino-groups (I):



(I.)



(II.)

It may be pointed out, however, that a representation in accordance with Sudborough and Beard's suggestion (p. 1273) brings the nitroamine group into close proximity with the amino-group. If the amine be represented as possessing a hemi-quinonoid structure, the intense colour of the molecular compounds and the comparative stability of the derivatives of secondary amines may also be explained. Thus the molecular compound with methylaniline might be represented as (II).

The influence of substituents in the phenyl group of the amine on the ease with which condensation can take place is not obvious in a formula of this type, whereas in the case of the Werner formula such substituents may be represented as modifying the amount of residual valency, whereby the amine is attached to the nitro-group.

We desire to thank Mr. Talfryn James for assistance in the preparation of some of the substances described.

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[Received, September 13th, 1920.]

### (XXXVIII).—*The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. Part II.*

By EDWARD BRADFORD MAXTED.

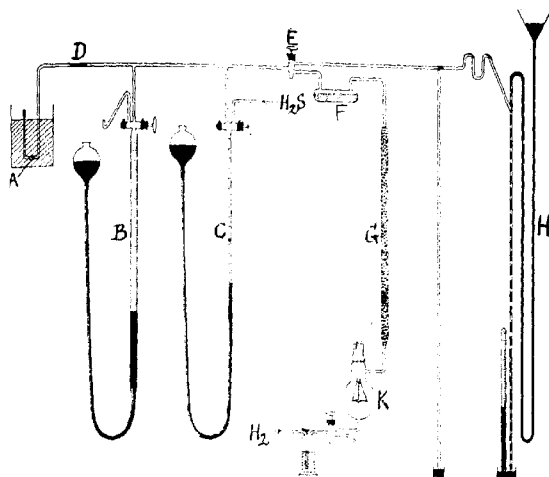
In a previous paper (T., 1919, 115, 1050) it has been shown that whilst comparatively small quantities of occluded hydrogen sulphide are sufficient totally to inhibit the subsequent occlusion of hydrogen by palladium, this occluded hydrogen sulphide, on being heated to 100° in a vacuum, evolves an equal volume of hydrogen and passes into a sulphur complex which is far less poisonous than hydrogen sulphide itself. The inhibitive effect of sulphur in the latter form could be predicted by assuming the formation of a complex  $\text{Pd}_2\text{S}$ , which is incapable of occlusion, and ascribing to the residual palladium its normal occlusive power for hydrogen.

In the previous paper, the minimum volume of hydrogen sulphide, as such, required for the complete inhibition of the occlusive power of palladium for hydrogen, was not determined, it being noted, however, that the volume of gas absorbed by palladium on exposure for a short time to hydrogen sulphide, this amounting in an experiment to 13.5 c.c. per gram of metal.

was sufficient to prevent the ordinary occlusion of hydrogen on subsequently admitting the gas.

The subject has now been investigated further, with the object of following quantitatively the inhibitive effect of successive increments in the hydrogen sulphide content of a given weight of palladium, this hydrogen sulphide being present in the form in which it is originally occluded and being added to the palladium in small known quantities, which for the majority of the measurements were less than the volume required for saturation. The poisoning curve for undecomposed occluded hydrogen sulphide was

FIG. 1.



found to be linear in form. Evidence was also obtained of the gradual and spontaneous dissociation of the occluded hydrogen sulphide even at the ordinary temperature, with the formation of hydrogen and of the  $\text{Pd}_4\text{S}$  complex. This reaction is accompanied by a corresponding change in the occlusive power.

#### EXPERIMENTAL.

The apparatus employed is shown diagrammatically in Fig. 1. It consists of a small absorption tube, *A*, containing a known weight of palladium, which was weighed out as chloride and reduced *in situ*, as before. In order to introduce into the system hydrogen



or hydrogen sulphide, as required, two gas burettes, *B* and *C*, were provided. These had a capacity of 25 c.c. and 5 c.c. respectively, the larger burette being employed for hydrogen. The system could be exhausted by means of a Sprengel pump, *H*, or, where more convenient, by lowering and raising the mercury in *B*, the three-way cock being turned as required. All parts of the apparatus were joined by fusion, and all stopcocks were mercury-sealed. In view of the inhibitive effect of mercury on the occlusive power of palladium observed by Paal and Hartmann (*Ber.*, 1918, 51, 711), a short plug of gold leaf, *D*, was inserted as a precaution against the possible penetration of traces of mercury vapour into the absorption tube. The hydrogen used for reducing the palladium chloride in *A* and for filling *B* was obtained from a cylinder of the electrolytic gas, and was freed from traces of oxygen by passage through a "half-watt" lamp, *K*, followed by a soda-lime tube, *G*, and phosphoric oxide tube, *F*. The hydrogen sulphide was prepared by the action of heat on magnesium hydrosulphide, and was dried by passage over calcium chloride. In order to reduce the volume of the absorbing system to as small a value as possible, capillary connexions were employed throughout. The volume of this system was redetermined for each absorption tube, the value being required in order to obtain the true occlusive power of the preparation from the volume of hydrogen absorbed from *B*.

Each measurement was begun by sealing on a fresh absorption tube containing a known weight of palladium chloride. This was reduced to metal by means of hydrogen at 100°, the current of gas passing out of the system by way of the open end of *A*, which was subsequently sealed off. The volume of hydrogen which was capable of being evolved at 100° or occluded at the ordinary temperature having been determined, as before, *A* was exhausted at 100°, and, after cooling to the ordinary temperature, *E* was closed and a known small volume of hydrogen sulphide allowed to pass from *C* into the absorption tube. This gas was found to be quickly and practically completely absorbed by the palladium, and, on subsequently admitting hydrogen from *B*, occlusion of this gas took place to an extent dependent on the degree of poisoning which had been induced by the preliminary treatment with hydrogen sulphide.

The results of the various measurements are summarised in table I, in which the experiments are arranged in order of increasing hydrogen sulphide content. The volumes of gas are in every case reduced to 0° and 760 mm., the experiments being, however, carried out at 20°.

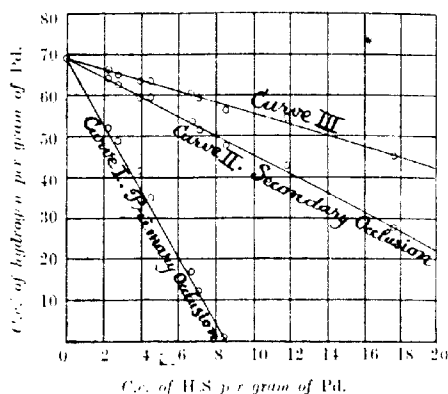
TABLE I.

No. of expt.	Weight of palladium, Gram.	Original occlusive power, C.c. H <sub>2</sub>	Equivalent occlusive power in C.c. H <sub>2</sub> per gram Pd.	C.c. H <sub>2</sub> S, absorbed.	C.c. H <sub>2</sub> S per gram Pd.	Subsequent primary occlusion, C.c. H <sub>2</sub>	Equivalent occlusive power in C.c. H <sub>2</sub> per gram Pd.	Total occlusion, C.c. H <sub>2</sub>	Total occlusive power per gram Pd.
1	0.1033	7.25	70.0	0.23	2.2	6.1	52.0	6.6	64.0
2	0.2380	16.45	69.2	0.65	2.74	11.7	49.0	14.85	62.5
3	0.0976	6.85	70.1	0.38	3.9	4.1	41.7	5.8	59.5
4	0.1714	12.1	70.5	0.78	4.56	6.0	35.0	10.25	59.8
5	0.2609	14.1	70.5	1.35	6.75	3.4	17.0	10.75	53.7
6	0.2795	19.0	68.0	2.00	7.16	3.5	12.5	14.25	51.9
7	0.1890	13.1	69.3	1.61	8.52	0.2	1.1	9.05	47.8
8	0.1422	9.9	69.6	1.68	11.8	Nil	Nil.	6.1	43.0
9	0.0933	6.75	68.0	1.75	17.6	Nil	Nil.	2.75	27.7

It will be seen that the occlusive power of palladium for hydrogen is diminished progressively by the presence of increasing concentrations of hydrogen sulphide. Provided that the ratio of hydrogen sulphide to palladium is less than a certain critical quantity, a volume of hydrogen, varying with the concentration of the inhibitor, is occluded at once in a normal manner, as is the case with unpoisoned palladium. This primary process of practically instantaneous absorption is followed by a secondary process, during which a further quantity of hydrogen is gradually and slowly occluded. Evidence will be adduced later in the present paper that secondary absorption is due to dissociation of the occluded hydrogen sulphide.

On passing through a critical value of about 8.5 c.c. of hydrogen

FIG. 2.

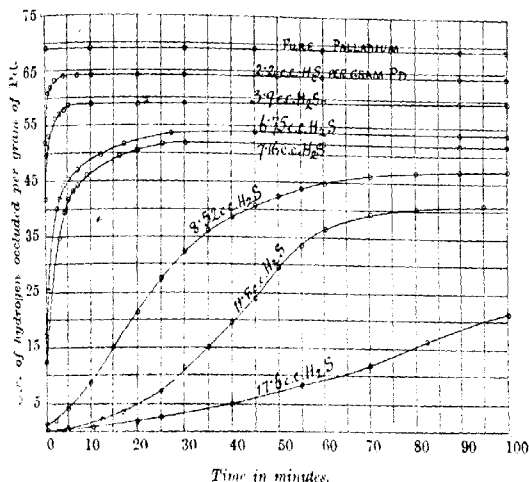


sulphide per gram of palladium, primary absorption ceases, and secondary occlusion only is observed; further, on plotting occlusive power against hydrogen sulphide content, it is seen that the influence of this inhibitor, both on primary occlusion and on total occlusion, is linear in nature. This result, which is analogous to that obtained for decomposed hydrogen sulphide, is illustrated in Curves I and II in Fig. 2.

In cases where the concentration of hydrogen sulphide is considerably in excess of that necessary totally to inhibit primary occlusion, the first stages of secondary absorption may take place sufficiently slowly to mask the process unless the system is kept under observation for a considerable time after admission of hydrogen. The process of secondary absorption, after beginning

slowly, gradually increases in velocity, and finally the velocity diminishes to zero as the limit of total occlusion is approached. With concentrations of hydrogen sulphide below the critical ratio, secondary absorption may, on the other hand, take place at a velocity sufficient to render necessary a very careful following of the movement of the mercury in the hydrogen burette, in order to map accurately the progress of the first stages of the process and to differentiate it from primary absorption. Measurements, in which readings of the volume occluded were taken, in such cases, every few seconds during the first stages of secondary occlusion,

FIG. 3.



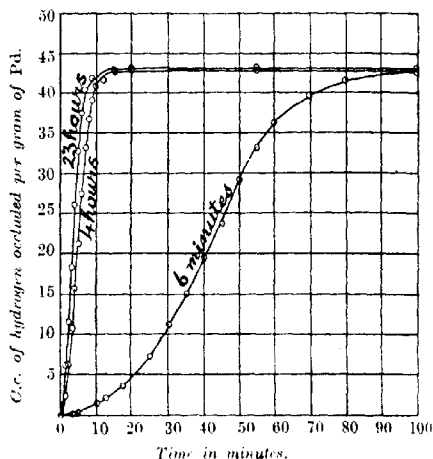
ave. however, shown that the general form of this absorption curve, although more rapid, is similar to that observed with higher concentrations of hydrogen sulphide, in which secondary occlusion is slower and more easily followed. The form of the various absorption curves is well shown in Fig. 3, in which the progress of absorption of certain of the measurements is plotted against the time.

In order to obtain information respecting the nature of the process involved during secondary occlusion, careful analyses were made of the gas remaining in the absorption pipette after secondary absorption had taken place, for the purpose of ascertaining whether

or not hydrogen sulphide is evolved during the change, simultaneously with the slow absorption of hydrogen. In no case was hydrogen sulphide in appreciable quantity observed, and exhaustion of the gas, followed by the introduction of fresh hydrogen, also failed to cause the fresh increase in occlusive power which would be expected if secondary occlusion were due either to the gradual displacement of hydrogen sulphide by hydrogen or to the reduction of a sulphide complex, with evolution of the sulphur as hydrogen sulphide.

The process appears, on the other hand, to be due to a change

Fig. 4.



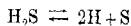
in the condition of the occluded hydrogen sulphide itself, in that the change in occlusive power is found to take place spontaneously on standing.

In order to investigate this point, three measurements were carried out with three specimens of palladium, which were in each case allowed to absorb about 11.8 c.c. of hydrogen sulphide per gram of palladium, the subsequent admission of hydrogen for the determination of the occlusive power being delayed for six minutes, four hours, and twenty-three hours respectively. The absorption curves obtained are reproduced in Fig. 4, from which it will be seen that whilst the final volume of hydrogen occluded by preparations containing an approximately equal volume of hydrogen sulphide is the same in each case, the form of the absorption curve

has been influenced by the time which has been allowed to elapse between treatment with hydrogen sulphide and subsequent measurement of the occlusive power for hydrogen, almost complete suppression of the slow process of secondary occlusion having been induced by allowing the system to stand.

The nature of the change undergone by occluded hydrogen sulphide during the comparatively slow passage of the system at 20° from a state of lower to one of higher occlusive power would seem to be similar to that obtained instantaneously at 100°, in which the hydrogen of the hydrogen sulphide has been shown to be evolved as such, the sulphur being retained by the palladium as a  $\text{Pd}_4\text{S}$  complex.

This view is supported by considering the dissociation reaction



in connexion with the volume of hydrogen occluded during primary and secondary absorption. During this dissociation, a volume of hydrogen equal, whilst in the molecular condition, to that of the hydrogen sulphide occluded is set free and must be added to the volume of hydrogen subsequently absorbed in order to derive the true occlusive power of the preparation. The total volume of hydrogen thus contained in the palladium should, if the reaction postulated is the correct one, fall on the known poisoning curve, calculated on the basis of the presence of  $\text{Pd}_4\text{S}$  complex in amount equal to the sulphur contained in the hydrogen sulphide occluded.

The close agreement between the observed occlusive powers and the values calculated from the  $\text{Pd}_4\text{S}$  curve is shown in table II, the results being also plotted graphically in curve 3 of Fig. 2.

TABLE II.

No. of expt.	C.c. $\text{H}_2\text{S}$ per gram palladium.	Hydrogen occluded. C.c.	Total hydrogen. C.c.	Total hydrogen calculated from $\text{Pd}_4\text{S}$ curve.
1	2.2	64.0	66.2	66.0
2	2.74	62.5	65.2	65.4
3	3.9	59.5	63.4	63.8
4	4.56	59.8	64.4	62.9
5	6.75	53.7	60.5	60.0
6	7.16	51.9	59.1	59.5
7	8.52	47.8	56.3	57.7
8	11.8	43.0	54.8	53.3
9	17.6	27.7	45.3	45.6

For the purpose of the calculation required for the above table, the occlusive power for hydrogen of 1 gram of unpoisoned palladium, under the given conditions, has been taken as 69 c.c., this value being in agreement both with the measurements

contained in the present paper and with those previously published.

The palladium, in addition to functioning as an occluding medium, would thus appear to induce the catalytic dissociation of the occluding hydrogen sulphide. This gradual dissociation affords also a ready explanation of the non-existence of a definite solubility of hydrogen sulphide in palladium. It has previously been shown that, after preliminary saturation, a slow but continuous absorption of hydrogen sulphide takes place, occlusion of as much as 42 c.c. per gram being observed by allowing palladium to remain for three weeks in excess of hydrogen sulphide. It will be seen that the gradual disappearance of occluded hydrogen sulphide, as such, due to the passage of the sulphur into the  $\text{Pd}_4\text{S}$  form, should cause the system to cease to be saturated for hydrogen sulphide. Fresh hydrogen sulphide is thus occluded, and the process continues until the occluding palladium has been eliminated as  $\text{Pd}_4\text{S}$  complex. It would be expected that the catalytic activity of the palladium, necessary for causing dissociation, would also decrease progressively as poisoning proceeds, so that the velocity of this dissociation, and consequently of the absorption of fresh hydrogen sulphide, should rapidly diminish with increase in the sulphur content of the palladium. This decrease in the velocity of the dissociation of hydrogen sulphide with increasing sulphur content is demonstrated in a striking manner by the curves of Fig. 3.

It should be emphasised that the complex  $\text{Pd}_4\text{S}$  cannot, without further investigation, be assumed to be a true sulphide of palladium, the character of this complex having yet to be determined.

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[Received, September 30th, 1920.]

### CXXXIX.—*Catalysis in the Hydrolysis of Esters by Infra-red Radiation.*

By ERIC KEIGHTLEY RIDEAL and JAMES ARTHUR HAWKINS.

ACCORDING to the quantum radiation hypothesis of chemical and physical actions as developed by Trautz, Lewis, and Perrin (compare *Ann. Physique*, 1919, [ix], 11, 5), molecules only become reactive after absorption of a definite amount of energy, the critical energy increment, although it appears probable that for

different reactions the degree of activation necessary may differ, yet these various stages of activation, corresponding with various critical energy increments, are related to one another in a simple manner. This energy acquired by the molecule is potential, and is assumed to be supplied by radiation; thus all reactions, in the broad sense of the term, are photochemical or photophysical. The chemical and physical effects produced by  $\alpha$ -particles and electrons may be included, since the characteristics of photochemical reactions may be quantitatively interpreted with the greatest facility on a corpuscular theory of radiation.

Up to the present time, with the exception of the photochemical reactions taking place in the actinic part of the spectrum, there has been no direct proof of the validity of the extension of this hypothesis into the other parts of the spectrum, especially the infra-red, the arguments in favour of such an hypothesis being indirect, based on experimental data, such as the temperature-coefficient of chemical and physical reactions, the heats of formation of chemical compounds, or the latent heat of evaporation of the elements.

The temperature-coefficient of methyl acetate has been studied in detail by Lamble and Lewis (T., 1914, 105, 2330), who found that the critical energy increment was about 17,000 calories per gram-molecule, which, on the quantum theory, would be provided by light of frequency of  $\nu = 1.6 \times 10^{14}$ , or wavelength  $\lambda = 1.9 \mu$  in the infra-red portion of the spectrum.

In a constant temperature enclosure, such as a thermostat, the density of the activating radiation,  $u_r$ , is constant, and the most convenient method of causing an alteration in  $u_r$ , and therefore of the reaction-velocity, is by alteration of the temperature.  $u_r$  can, however, be altered by either decreasing or increasing the absorbable radiation density without altering the mean temperature. Thus plants which are photosensitive to the actinic part of the spectrum practically cease growing in the dark, although maintained at the same temperature, and other typical photochemical and photocatalytic reactions behave in like manner. In the case of infra-red radiation, however, it is difficult to shield any part of the reacting system from radiation of any particular absorbable frequency, since the system itself can emit this radiation either as a result of intramolecular vibration or even intermolecular collisions (see Nernst, "Die Theoretischen und Exp. Grundlagen des neuen Wärmesatzes," Halle, 1918, p. 63). Alteration of the medium in which the reacting molecules are dispersed does, however, produce an alteration in the reaction velocity, but, as pointed out above, it is at present uncertain whether this is the result of



an alteration in  $u$ , the activating radiation density, or due to an alteration in  $\nu$  equivalent to an alteration in the activating radiation frequencies and the mechanism of the reaction, or to both factors.

It is, however, quite possible to increase the density of the activating radiation,  $\nu$ , by illumination with radiation of the correct wave-length,  $\lambda = 1.9 \mu$ . In the course of time, this radiation will be absorbed, and the energy will be equally distributed over the whole spectrum, resulting in an elevation of temperature, but if the reaction is truly photochemical and selectively absorbs radiation of this frequency, a marked acceleration in the reaction-velocity should result without an appreciable rise in temperature.

To test this point, a series of preliminary experiments was conducted on the rate of hydrolysis of methyl acetate dissolved in dilute hydrochloric acid and exposed to infra-red radiation; the velocity-coefficients obtained in this way were compared with the normal values obtained from identical solutions maintained in the dark.

#### EXPERIMENTAL.

As a source of infra-red radiation, preliminary experiments indicated that an arc lamp was unsuitable, since, although the carbon spectrum lines could be maintained at fairly uniform intensity, the infra-red portion of the spectrum (produced by the hot vapours) fluctuated in intensity. A uniform, although relatively feeble, infra-red beam was obtained from a small bundle of the oxide filaments commonly employed in the Nernst glow-lamp. A number of experiments were likewise conducted with a nichrome spiral raised to  $600^{\circ}$ ; the relatively large quantity of non-radiant heat proved, however, to be a serious disadvantage. The sun was found to be the most convenient source of suitable radiation. In all cases, the spectrum was obtained by dispersion through a simple optical system of lenses and quartz prism, a salt prism not being available. No attempt was made to select any narrow spectral beam, but that part of the spectrum was employed commencing with the portion of the red just beyond the visible and stretching to an indefinite extent into the infra-red. To eliminate as far as possible the material absorption of the radiation, and thus minimise the dissipation of the energy as heat, the methyl acetate was illuminated directly with the radiation without the intervention of any glass. The solution undergoing hydrolysis was contained in a 100 c.c. beaker covered on the outside with tinfoil, a similar beaker containing the control solution.

# HYDROLYSIS OF ESTERS BY INFRA-RED RADIATION. 1291

Both beakers were maintained at uniform temperature by immersion in a thermostat or in broken ice and water. The temperature of each solution was continually observed, and samples for analysis withdrawn at simultaneous intervals for titration with 0.054*N*-baryta. In all respects, except for illumination, both solutions were maintained under identical conditions and treated in the same manner.

In the following tables are given the data of a number of experiments and the velocity-coefficients therefrom.

Illuminant: Nernst Filaments.

Acid: 0.1987*N*-HCl. *k* calculated as a unimolecular constant.

(I.)

Time.		Control.		<i>k</i> × 10 <sup>4</sup> .	Illuminated.		<i>k</i> × 10 <sup>4</sup> .
Hrs.	Min.	Tempera- ture.	Titre. C.c.		Tempera- ture.	Titre. C.c.	
1	55	21.75°	7.36	—	21.75°	7.36	—
2	9	—	7.50	12.71	—	7.76	36.79
2	39	21.75	8.22	23.16	21.80	8.54	36.81
3	4	—	8.34	22.46	—	8.64	25.77
4	15	21.75	8.80	14.10	21.80	8.83	14.39
5	25	—	9.48	15.07	—	9.50	15.24
α	—	—	15.19	—	—	15.19	—

(II.)

12	46	20.9°	7.30	—	21.1°	7.20 (?)	26.00
12	58	22.3	7.34	7.39	22.3	7.45	31.67
1	14	23.4	7.37	6.00	23.7	7.65	41.35
1	31	23.7	7.45	9.26	23.85	8.00	41.09
1	46	24.9	8.01	25.22	24.7	8.38	41.69
(Time 2 hrs. 4 mins.)							
2	14	24.5	8.16	26.54	24.2	8.57	—
3	10	18.35	8.51	24.27	18.2	9.10	40.15
4	45	18.35	9.84 (?)	41.94	17.9	9.55	41.94
α	—	—	11.40	—	—	11.40	—

III.)

Time.		Titre. C.c.		Temperature.		<i>k</i> × 10 <sup>4</sup> .	
Hrs.	Min.	Control.	Illum- inated.	Control.	Illum- inated.	Control.	Illum- inated.
9	35	6.09	6.09	21.70	21.70	—	Dark.
9	49	6.26	6.25	21.70	21.70	19.66	19.66
10	7	6.50	6.57	21.30	21.30	20.04	26.22
10	49	7.08	7.38	21.20	21.25	22.99	30.83
11	49	7.31	7.67	20.75	20.75	16.42	18.21
1	0	8.46	8.79	20.75	20.80	23.39	27.78
α	—	12.21	12.21	20.75	20.75	—	—

Illuminant: Sunlight.

Time.		Temperature.		Titre. C.c.		$k \times 10^4$ .		Remarks.
Hrs.	Min. utes.	Control.	Illuminated.	Control.	Illuminated.	Control.	Illuminated.	
1	28	1.0°	1.0°	7.20	7.20	—	—	—
1	39	0.5	0.5	7.22	7.23	4.99	8.47	—
1	51	0.0	0.0	7.23	7.25	4.46	5.82	—
2	3	0.0	0.0	7.26	7.30	4.39	6.85	—
2	13	0.0	0.0	7.28	7.31	4.34	6.28	Sun clouded.
2	29	0.0	0.0	7.30	7.35	4.23	6.26	—
2	51	1.0	1.0	7.34	7.38	4.34	5.75	Sun clouded.
3	52	4.0	4.0	7.48	7.54	4.39	5.47	—
$\infty$		—	—	11.06	11.06	—	—	—

Illuminant: Sunlight and Nichrome Coil.

Time.		Temperature.			Titre. C.c.		
Hrs.	Min. utes.	Control.	Sun.	Nichrome.	Control.	Sun.	Nichrome.
1	50	4.0°	4.0°	14.0°	7.10	7.10	7.10.
2	3	2.0	4.0	11.0	7.13	7.15	7.17
2	12	1.5	2.5	11.5	7.18	7.28	7.35
2	23	1.5	2.5	11.0	7.23	7.28	7.37
2	53	1.5	2.5	11.0	7.25	7.30	7.62
3	14	1.5	2.5	11.0	7.25	7.30	7.67
6	9	1.5	2.5	11.0	7.70	7.81	8.49
$\infty$		—	—	—	13.29	13.29	13.29

Time.		$k \times 10^4$ .			Nichrome calculated on temperature basis.
Hrs.	Min. utes.	Control.	Sun.	Nichrome.	
1	50	3.84	—	—	—
2	3	4.89	12.21	18.97	9.02
2	12	4.93	12.29	18.49	12.23
2	23	3.80	7.41	13.48	11.90
2	53	2.37	5.34	13.82	9.19
3	14	4.05	3.34	9.61	5.73
6	9	—	4.85	10.12	5.27

It is evident that the illuminated methyl acetate is hydrolysed much more rapidly than that maintained at the same temperature in the dark.

That the variability in the velocity-coefficient of the illuminated reactants is chiefly due to an alteration in the intensity of the infra-red radiation was evident from the obvious alteration in the intensity of the sunlight by the passage of clouds. To control this factor, experiments were conducted in which the rate of liberation of iodine by catalytic atmospheric oxidation from acidified potassium iodide was simultaneously measured. This reaction is a typical photochemical one. It is evident from the following figures that the same factor, namely, the radiation intensity, affects both reactions, an alteration in the velocity-coefficient of one reaction coinciding approximately with a similar alteration in the other.

Illuminant: Sun.		Time.	Titre. C.c.		Temperature.		$k \times 10^4$ .	Milligram of iodine liberated per minute.	Remarks.
Hrs.	Mins.		Control.	Illuminated.	Control.	Illuminated.			
1	38		5.90	5.90	9.0	9.0	3.32	—	Both dark.
1	53		5.93	5.93	3.0	3.5	3.33	—	Both dark.
2	9		5.96	6.03	0.5	0.5	3.03	7.61	Both dark.
2	23		6.00	6.08	0.5	0.5	3.68	5.53	Illuminated.
2	40		6.02	6.10	0.5	0.5	3.38	—	—
3	1		6.06	6.16	2.0	2.0	—	—	—
3	22		6.11	6.20	1.0	1.0	3.47	5.47	—
3	41		6.13	6.23	1.0	0.5	3.21	5.03	—
$\infty$			9.73	10.90	—	—	—	0.0045	—
								0.0026	—
								4.48	—
1	12		5.88	5.82	6.0	9.0	2.78	3.49	Dark.
1	26		5.90	5.85	1.0	3.0	2.69	12.90	Illuminated.
1	46		5.93	6.05	1.0	1.0	2.48	9.93	—
2	9		5.95	6.08	1.0	0.5	3.68	6.51	—
2	17		6.02	6.11	1.0	1.0	3.05	0.0033	—
2	21		6.02	6.10	1.0	1.0	2.94	6.76	—
2	46		6.05	6.17	1.0	1.0	—	—	—
$\infty$			11.00	11.14	—	—	—	—	—

Illuminant: Sun. Temperature, 0°.

Time.		Control.		Illuminated.		Milligram of iodine liberated per minute.
Hrs.	Mins.	Titre, C.c.	$k \times 10^4$ .	Titre, C.c.	$k \times 10^4$ .	
2	35	5.75	1.87	5.75	—	—
2	51	5.77	2.06	5.85	9.92	0.0043
3	8	5.81	3.70	5.86	4.11	0.0025
3	33	5.88	4.36	5.90	4.39	0.0025
3	51	5.95	—	5.97	5.99	0.0030
$\alpha$		11.85	—	11.85	—	—

It seemed possible that the radiation, falling on the surface of the methyl acetate solution, would produce a local rise of temperature, and that the heat would be carried by conduction to the walls of the vessel before the whole body of the solution acquired a higher temperature; thus local rapid hydrolysis might be produced. This possibility was, in reality, remote, since the solution was frequently agitated, and no difference in temperature was observed. Nevertheless, it was thought desirable to test this point experimentally. A small vessel containing oil, which could be maintained at any desired temperature by means of an electric resistance immersed in it, was lowered just under the surface of the methyl acetate solution, and sufficient energy was supplied to the oil to maintain the methyl acetate about 0.5° higher than the control experiment.

The velocity-coefficients obtained in this way agreed very closely with those calculated from the control experiments after correction for a rise in temperature of 0.6°, as is evidenced from the following values:

$k \times 10^4$ observed .....	2.13	3.98	3.73	3.92	3.96
$k \times 10^4$ calculated.....	2.13	3.99	3.73	3.86	3.96

From these experiments, it would seem that the hydrolysis of methyl acetate is in reality accelerated by irradiation in the infra-red portion of the spectrum, an interesting example of infra-red photochemical action; furthermore, that this spectral region is the region of activity anticipated by the application of the activation and quantum theories to chemical change.

It is hoped to continue and extend these experiments in the near future in order, if possible, to elucidate the mechanism of the catalytic activity of the acid employed. There are two tenable theories to explain this catalytic activity, either by an increase in the activating radiation density or by an alteration in the mechanism of the reaction.

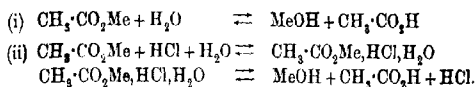
Although the above experimental data, limited to one acid concentration, are too limited to draw any definite conclusion, it would appear probable that the second hypothesis, namely, an alteration

in the mechanism of the reaction, that is, the intermediate compound theory of catalysts, is the correct one.

It will be noted that during the first period of illumination there is a very remarkable increase in the velocity-coefficient, and that subsequently the rate of reaction diminishes to a fairly constant value, which is, however, still greater than that of the unilluminated sample.

This phenomenon is not readily intelligible on the assumption of the action of the acid as affecting a simple increase in the radiation density, since a further increase in the radiation density should increase the reaction velocity *pro rata*. On the intermediate-compound theory, however, the observed result is to be anticipated.

Briefly, if the two reactions be represented by the following purely hypothetical equations:



the rate of decomposition in each case being unimolecular in excess of water, then the first reaction-velocity is governed by the rate of activation of the methyl acetate to react with the active water, and the second by two reactions, namely, the rate of activation of the methyl acetate to react with active hydrochloric acid, and by the rate of activation of the complex to break down into the products of the reaction. The rate of any sequent reaction is always governed by the slowest of the intermediate reactions; thus, if we assume the slowest one in this case to be the decomposition of the complex, then illumination with a particular frequency of light will accelerate the decomposition of the complex, so that the reaction-velocity will then be governed by the next slowest reaction, which we have assumed to be the combination of the methyl acetate and hydrated hydrochloric acid. This reaction, however, takes place more rapidly than the combination of methyl acetate and water. On this hypothesis of series reactions, the primary acceleration on illumination is to be attributed to the rapid decomposition of the complex, which is present in relatively large quantities, since it breaks down but slowly; the primary accelerates, then falls off until the normal rate of the next slowest reaction sets in.

#### Summary.

Preliminary experiments have indicated that the hydrolysis of methyl acetate is catalytically accelerated by infra-red radiation.

The spectral region of photoactivity is in agreement with that calculated on the activation and quantum theories of chemical action.

The experimental data obtained are most readily interpreted on the intermediate-compounds hypothesis in the case of the hydrolysis of esters by dilute acids. It is proposed to extend these experiments in order to obtain further information as to the number and nature of these intermediate compounds, and to examine the spectral region of their activation in more detail.

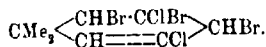
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[Received, July 15th, 1920.]

### CXL.—The Action of Chlorine on 3:5-Dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene.

By LEONARD ERIC HINKEL.

In the study of the conversion of hydroaromatic derivatives into compounds of the aromatic series, the action of bromine on 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene was fully investigated (Crossley, T., 1904, **85**, 264). It was shown that the reaction was largely influenced by condition of experiment, 2 molecules of bromine giving rise to a viscid liquid, which, on distillation, gave 3:5-dichloro-4-bromo-*o*-xylene and a crystalline solid,  $C_8H_6Cl_2Br_2$ , presumed to be dichlorotribromodimethylcyclohexene,

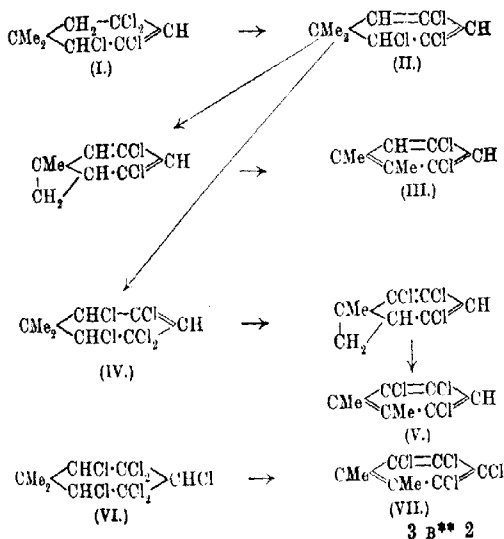


On the other hand, 1 molecule of bromine gave as principal product 3:5-dichloro-6-bromo-*o*-xylene. Explanations of the production of the various substances are suggested in the original paper, but as several points remained to be cleared up, the work was repeated, using chlorine instead of bromine, in the hope that more light would be thrown on the mechanism of this type of reaction.

When 3:5-dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene is treated with chlorine, the product consists of a viscous syrup, which yields a small quantity of a crystalline solid,  $C_8H_6Cl_3$ . The syrupy filtrate from the crystals yields, on distillation, the two isomeric trichloro-*o*-xylenes, and also tetrachloro-*o*-xylene. The compound  $C_8H_5Cl_5$  is evidently a *pentachlorodimethylcyclohexene*, corresponding with and formed in a manner similar to the dichlorotribromodimethylcyclohexene described by Crossley (*loc. cit.*), and in like manner accounts for the formation of 3:4:5-trichloro-*o*-xylene if

3:5-DICHLORO-1:1-DIMETHYL- $\Delta^{2:4}$ -CYCLOHEXADIENE. 1297

the filtrate from the crystals, since the pentachloro-compound decomposes on heating into 3:4:5-trichloro-*o*-xylene. The formation of pentachlorodimethylcyclohexene does not, however, account for the production of either 3:5:6-trichloro-*o*-xylene or tetrachloro-*o*-xylene. The action of chlorine on dichlorodimethylcyclohexadiene must be more deep-seated, since 100 grams of the latter yield only 28 grams of pentachlorodimethylcyclohexene, 18–20 grams of 3:5:6-trichloro-*o*-xylene, and 10–12 grams of a mixture of 3:4:5-trichloro-*o*-xylene and tetrachloro-*o*-xylene. Moreover, when 1 molecule of chlorine acts on dichlorodimethylcyclohexadiene, the resulting liquid always contains a considerable quantity of the unchanged original compound, together with 3:5-di- and 3:5:6-trichloroxylens; the yield of 3:5:6-trichloro-*o*-xylene is small, being only 16–18 grams from 100 grams of dichlorodimethylcyclohexadiene. The product of the action of one molecular proportion of chlorine on dichlorodimethylcyclohexadiene is probably tetrachlorodimethylcyclohexene (I); this substance is unstable, and very readily evolves hydrogen chloride even at low temperatures, probably forming a trichlorodimethylcyclohexadiene (II), which then slowly loses another molecule of hydrogen chloride, yielding 3:5-dichloro-*o*-xylene (III). A compound of formula II would combine with 1 molecule of chlorine in a manner similar to dichlorodimethylcyclohexadiene, yielding





an unstable substance (IV), from which, by loss of 1 molecule of hydrogen chloride, 3:5:6-trichloro-*o*-xylene (V) would result.

The formation of tetrachloro-*o*-xylene can be explained by supposing that with excess of chlorine the two compounds II and IV are successively formed, and that more chlorine combines with IV, yielding an unstable substance having the formula VI, which immediately loses hydrogen chloride, giving rise to tetrachloro-*o*-xylene (VII).

The only point to be decided is the position of the chlorine atoms in the two possible trichloro-*o*-xylenes. 3:4:5-Trichloro-*o*-xylene was therefore synthesised from *o*-4-xylidene, which was chlorinated, and the amino-group then displaced by chlorine. The 3:4:5-trichloro-*o*-xylene obtained in this way melted at 96°, and its melting point remained unchanged when mixed with the substance obtained by heating pentachlorodimethylcyclohexene. Consequently, the other trichloro-*o*-xylene must have the chlorine atoms in the 3:5:6-position.

Both the trichloro-*o*-xylenes yield on further chlorination the same tetrachloro-*o*-xylene, melting at 223–224°, which was identical with the compound obtained by the action of nitric acid on pentachlorodimethylcyclohexene, and also with the substance, melting at 223–224°, isolated in the distillate obtained from the filtrate from pentachlorodimethylcyclohexene.

3:4:5-Trichloro-*o*-xylene on bromination readily yields 3:4:5-trichloro-6-bromo-*o*-xylene, but on brominating 3:5:6-trichloro-*o*-xylene in a similar manner, an unexpected reaction takes place, giving rise to 3:5-dichloro-4:6-dibromo-*o*-xylene, and not 3:5:6-trichloro-4-bromo-*o*-xylene.

Both the trichloro-*o*-xylenes resemble the dichlorobromo-*o*-xylenes in their behaviour towards nitric acid. Thus, 3:4:5-trichloro-*o*-xylene gives with fuming nitric acid 3:4:5-trichloro-6-nitro-*o*-xylene, whereas 3:5:6-trichloro-*o*-xylene under similar treatment gives 3:5-dichloro-4:6-dinitro-*o*-xylene.

#### EXPERIMENTAL.

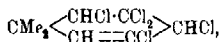
##### *Action of Excess of Chlorine on 3:5-Dichloro-1:1-dimethyl-Δ<sup>2</sup>-4-cyclohexadiene.*

Seventy grams of freshly prepared dichlorodimethylcyclohexadiene were dissolved in 70 grams of dry chloroform, and a rapid stream of chlorine was passed in, the whole being cooled in ice. Hydrogen chloride was immediately evolved, and subsequently in torrents. After saturation with chlorine, the chloroform was evaporated on the water-bath, and the viscid, yellow

### 3:5-DICHLORO-1:1-DIMETHYL- $\Delta^{3:4}$ -CYCLOHEXADIENE. 1299

liquid was placed in a vacuum over sodium hydroxide, when it gradually deposited colourless crystals. These were collected (18.5 grams) (filtrate=*A*), and, after being rapidly washed with light petroleum, purified by crystallisation from alcohol (Found: Cl=62.62.  $C_8H_2Cl_2$  requires Cl=62.83 per cent.).

2:3:3:4:5-Pentachloro-1:1-dimethyl- $\Delta^5$ -cyclohexene,



is readily soluble in the cold in ether, chloroform, acetone, benzene, or methyl and ethyl alcohols, and in light petroleum on warming. It crystallises in stout, prismatic needles melting at 103.5°.

#### *Action of Heat on Pentachlorodimethylcyclohexene.*

The substance was heated at 120–130° in a sulphuric acid bath, when it melted to a colourless liquid, and copious evolution of hydrogen chloride occurred. The liquid was then removed from the acid-bath and heated more strongly until no further evolution of hydrogen chloride occurred and the liquid began to boil. The residue solidified on cooling, and was crystallised from alcohol (Found: Cl=51.16. Calc.: Cl=50.83 per cent.).

3:4:5-Trichloro-*o*-xylene is very readily soluble in ether, chloroform, benzene, light petroleum, or hot alcohol, crystallising from the latter in masses of felt-like needles, which, on pressing, form a waxy mass melting at 96°. It distils unchanged at 261°, is volatile in steam, and is evidently identical with the compound described by Claus and Kautz (*Ber.*, 1885, **18**, 1369), who give m. p. 93° and d. p. 265°.

On chlorination and bromination in the presence of iron, it gives, respectively, 3:4:5:6-tetrachloro-*o*-xylene melting at 223–224° (p. 1300) and 3:4:5-trichloro-6-bromo-*o*-xylene melting at 226° (p. 1300). Fuming nitric acid converts it into 3:4:5-trichloro-6-nitro-*o*-xylene melting at 149° (p. 1301).

#### *Action of Nitric Acid on Pentachlorodimethylcyclohexene.*

Five grams of the cyclohexene derivative were heated with 40 c.c. of fuming nitric acid over a water-bath. A vigorous action ensued, and, after heating for ten minutes, the contents of the flask were poured into cold water. The pasty solid was collected, washed with water, and, after three crystallisations from ethyl acetate, the needles melted at 223–224°; the melting point was not altered on mixing with 3:4:5:6-tetrachloro-*o*-xylene (p. 1300) (Found: Cl=58.4. Calc.: Cl=58.19 per cent.).

*Examination of Filtrate A (p. 1299).*

The liquid was heated in a distilling flask to 140° and gradually raised to 180°; a copious evolution of hydrogen chloride occurred. The liquid was maintained at 180—200° for one hour, and then gently distilled, three main fractions being obtained boiling at 225—245°, 245—260°, and 260—270°. The first two fractions, which partly solidified on keeping, were subjected to careful and repeated fractional distillation, and the main fraction, b. p. 230—240°, solidified completely, on cooling, to a colourless, crystalline mass, which, after being crystallised several times from alcohol, melted sharply at 47.5°, and consisted of 3:5:6-trichloro-o-xylene (p. 1302) (Found: Cl=50.99.  $C_8H_7Cl_3$  requires Cl=50.83 per cent.).

The residue of higher boiling point was added to the third fraction (b. p. 260—270°), and on submitting the mixture to repeated fractional distillation, two main fractions, b. p. 255—265° and 275—280°, were obtained. These were subjected to repeated fractional crystallisation from alcohol, and then from ethyl acetate, in which the fraction of higher boiling point is less readily soluble, and a partial separation was effected yielding two substances, one crystallising from alcohol in felt-like needles melting at 96°, and at the same temperature when mixed with 3:4:5-trichloro-o-xylene (p. 1299), the other crystallising from ethyl acetate in long, transparent needles melting at 223—224°, and at the same temperature when mixed with 3:4:5:6-tetrachloro-o-xylene (below).

*Action of Chlorine on 3:4:5-Trichloro-o-xylene: Formation of 3:4:5:6-Tetrachloro-o-xylene (VII).*

Two grams of the substance were dissolved in 10 c.c. of dry chloroform, and chlorine was rapidly passed into the solution in the presence of a small quantity of iron filings. On warming, substitution readily took place. The chloroform was evaporated and the residue crystallised from ethyl acetate. The substance is very readily soluble in ether, and readily so in chloroform, hot alcohol, or ethyl acetate, crystallising from the latter in long, slender, glistening needles melting at 223—224° (Claus and Kautz, *loc. cit.*, give 215°).

*Action of Bromine on 3:4:5-Trichloro-o-xylene: Formation of 3:4:5:6-Tetrachloro-6-bromo-o-xylene.*

The substance was dissolved in a small quantity of chloroform and bromine added in the presence of iron filings. On warming

### 3:5-DICHLORO-1:1-DIMETHYL- $\Delta^{2:4}$ -CYCLOHEXADIENE. 1301

substitution took place, and the sparingly soluble bromo-derivative separated. The chloroform was evaporated and the residue dissolved in benzene, the solution being washed with water, dried, concentrated, and allowed to crystallise (Found: Cl=36.67; Br=28.05.  $C_8H_6Cl_2Br$  requires Cl=36.92; Br=27.73 per cent.).

The compound is readily soluble in ether or benzene, sparingly so in chloroform or alcohol, and crystallises from ethyl acetate in slender, glistening needles melting at 226°.

#### *Action of Nitric Acid on 3:4:5-Trichloro-o-xylene: Formation of 3:4:5-Trichloro-6-nitro-o-xylene.*

Four grams of the substance were gradually added to 40 c.c. of fuming nitric acid and warmed on the water-bath for twenty minutes, when the solid gradually dissolved. The mixture was poured into water, and the separated solid crystallised from alcohol, in which it is sparingly soluble (Found: N=5.436.  $C_8H_6O_2NCl_3$  requires N=5.5 per cent.).

The compound is readily soluble in ether, acetone, benzene, chloroform, or light petroleum, and moderately so in hot alcohol or hot glacial acetic acid; it crystallises from alcohol in stout, transparent crystals possessing a slight yellow tinge, and melting at 149°.

#### *Synthesis of 3:4:5-Trichloro-o-xylene.*

*o*-4-Xylidine was acetylated and chlorinated as described by Crossley (*loc. cit.*). Three grams of the resulting 3:5-dichloro-*o*-4-xylidine were suspended in 15 c.c. of concentrated hydrochloric acid, in which it is not soluble in the cold, a solution of 1.5 grams of freshly prepared cuprous chloride in 15 c.c. of concentrated hydrochloric acid was added, and a solution of 1.1 grams of sodium nitrite in the least amount of water dropped into the mixture, which was heated on a water-bath to 60–70°. After one hour, the whole was distilled in a current of steam, when a solid passed over which melted at 82°. After recrystallising twice from alcohol, the crystals melted sharply at 96°, and the melting point was not changed when the substance was mixed with the trichloro-*o*-xylene described on p. 1299.

#### *Action of One Molecular Proportion of Chlorine on 3:5-Dichloro-1:1-dimethyl- $\Delta^{2:4}$ -cyclohexadiene.*

Dichlorodimethylcyclohexadiene (1 mol.) was dissolved in twice its weight of dry chloroform, and the solution cooled in a freezing mixture of ice and salt. Chlorine was passed into the mixture,

and the hydrogen chloride, which was immediately evolved, absorbed in a soda-lime tube. The passage of chlorine was stopped when the increase in total weight of the apparatus was equivalent to one molecular proportion of chlorine. On evaporating the chloroform, a pale yellow liquid remained which showed no signs of crystallisation, even after remaining for a long time in a vacuum over sodium hydroxide. The liquid was heated to  $150\text{--}180^\circ$  for one hour, when much hydrogen chloride was evolved. The liquid was then distilled, and a clear, yellow liquid, boiling between  $215^\circ$  and  $241^\circ$ , passed over. The liquid was submitted to careful and repeated fractional distillation, and three fractions, boiling at  $217\text{--}220^\circ$ ,  $222\text{--}226^\circ$ , and  $228\text{--}233^\circ$ , were collected.

*Fraction b. p.  $217\text{--}220^\circ$ .*—This liquid, when left in the air, rapidly darkened and resinified, and when hydrolysed with 30 per cent. sulphuric acid yielded dimethyldihydroresorcin, showing that it contained 3:5-dichloro-1:1-dimethylcyclohexadiene.

*Fraction b. p.  $222\text{--}226^\circ$ .*—This liquid could not be separated into a portion boiling constantly at  $226^\circ$  (3:5-dichloro-*o*-xylene). When treated with bromine in the presence of iron filings, it gave 3:5-dichloro-4:6-dibromo-*o*-xylene, which, after crystallisation from ethyl acetate, melted at  $233^\circ$  (compare Crossley, *loc. cit.*, p. 284), and on nitration gave 3:5-dichloro-4:6-dinitro-*o*-xylene melting at  $173\text{--}174^\circ$ , and identical with the compound obtained by the action of nitric acid on 3:5:6-trichloro-*o*-xylene (p. 1303).

*Fraction b. p.  $228\text{--}233^\circ$ .*—The liquid almost entirely solidified on cooling. The crystals were collected and the filtrate was dissolved in warm alcohol, and the solution cooled in ice, when a further yield of crystals was obtained, which, after crystallising several times from alcohol, melted at  $47.5^\circ$ . This melting point was not altered when the substance was mixed with 3:5:6-trichloro-*o*-xylene (p. 1300).

3:5:6-Trichloro-*o*-xylene is readily soluble in the cold in ether, benzene, chloroform, light petroleum, or ethyl acetate, crystallises from methyl or ethyl alcohol in short, colourless crystals, and can be distilled unchanged. It is readily acted on by chlorine in the presence of iron filings; the solid product crystallises from ethyl acetate in long, glistening needles melting at  $223\text{--}224^\circ$ , and is identical with 3:4:5:6-tetrachloro-*o*-xylene (p. 1300).

#### *Action of Bromine on 3:5:6-Trichloro-*o*-xylene.*

Two grains of the substance were dissolved in 10 c.c. of dry chloroform, and excess of bromine was added in the presence of iron filings. On warming, substitution takes place readily. The

solid product crystallised from ethyl acetate in long, silky needles melting at  $233^{\circ}$ , and this melting point was not changed when the substance was mixed with 3:5-dichloro-4:6-dibromo-*o*-xylene (Found: Cl=21.65; Br=47.63. Calc.: Cl=21.32; Br=48.05 per cent.).

*Action of Nitric Acid on 3:5:6-Trichloro-o-xylene.*

Five grams of the substance were slowly added to 30 c.c. of fuming nitric acid and warmed on the water-bath, when the solid dissolved, after which a rather vigorous action took place. The heating was continued for twenty-five minutes, the mixture poured into cold water, and the separated semi-solid, after being washed with warm water, crystallised from alcohol. Considerable difficulty was experienced in purifying this material by means of alcohol, and it was therefore twice recrystallised from light petroleum (b. p.  $40-60^{\circ}$ ) and finally from alcohol. The flat plates obtained in this way melted at  $174^{\circ}$ , and were identified as 3:5-dichloro-4:6-dinitro-*o*-xylene (Crossley, *loc. cit.*, p. 284) (Found: N=10.51. Calc.: N=10.56 per cent.).

The author wishes to express his indebtedness to Colonel A. W. Crossley, C.M.G., for suggesting the above investigation and for much valuable help and advice throughout; thanks are also due to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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[Received, September 24th, 1920.]

## CXLI.—*The Effect of Asymmetry. A Study in Crystal Structure.*

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COMPARATIVE studies of more or less closely related organic compounds abound in the literature of crystallography; in fact, the attempt to trace so-called "morphotropic resemblances" may be regarded as one of the distinctive features of crystallographic investigation during the last fifty years. Whilst such investigations have added extensively to the general stock of knowledge, they cannot, unfortunately, be said to have led to the formula-

tion of any general laws correlating chemical composition and crystalline form. At least one of the causes of this general failure has been recently revealed as the result of the investigation of crystal structure by means of X-rays. It is now clear that the Bravais space-lattices do not always represent completely the structure of a crystal, for something like 70 per cent. of the structures already elucidated by X-ray methods consist of several interpenetrating space-lattices, that is, of "point systems" in the sense of Sohncke, Fedorov, and Schönflies. Crystal structure is thereby proved to be a subject of great complexity, and much further investigation is evidently needed before general laws can be formulated.

The object of the present research was to ascertain whether a definite similarity may exist between the crystalline forms of two closely related organic substances, one of which differs from the other in possessing an asymmetric atom. The kind of similarity sought was of that definite degree which exists between isomorphous substances rather than that vaguely implied by a "morphotropic resemblance."

In selecting materials for examination, it was necessary to find a series of compounds in which the replacement of one radicle by another is not incompatible with an isomorphous relationship (at least so long as the molecule remains symmetrical) before proceeding to inquire whether a further replacement of radicles, by which the molecule becomes asymmetric, is compatible with the survival of isomorphism. Now, experience shows that in series involving the replacement of organic radicles, isomorphism is only to be found where the molecule is relatively large in proportion to the change of composition, and it therefore seemed probable that compounds of the type  $R_4NHgI_3$  (that is, "double compounds" of a quaternary ammonium iodide with mercuric iodide in the ratio 1:1), in which R may represent either identical or different organic radicles, should be suitable for the end in view. Such compounds, having a pale to deep lemon-yellow colour, are known to crystallise well from acetone solutions. A commencement was therefore made with a series of compounds in which  $R_4$  is wholly represented by alkyl groups (compare table I), but no definite cases of isomorphism were encountered. This is a fact of some significance, as illustrating the highly sensitive character of the relationship between form and composition: in spite of the high molecular weight, the replacement of even a single methyl by an ethyl radicle brings about a fundamental change of crystalline form and structure.

The investigation of a still more complex group then became necessary. The phenylalkylammonium compounds, of the general

TABLE I.  
*The Alkylammonium Group of Compounds.\**

No.	Substance.	System.	Crystallographic constants.			Prism angle.	Cleavage.
			$a : b : c$	Axial angles.			
1	$\text{Me}_2\text{NHgI}_2$	Rhombic	0.5777 : 1 : 0.5199	—		60° 2'	(001) imperfect.
2	$\text{MeEt}_2\text{NHgI}_2$	Anorthic	1.1202 : 1 : 0.5578	$\alpha = 102^\circ 55'$ $\beta = 93^\circ 56'$ $\gamma = 108^\circ 25'$		98° 18'	(110) good. ( $\bar{1}\bar{1}0$ ) good.
3	$\text{Et}_2\text{NHgI}_2$	Monoclinic	1.4826 : 1 : 0.8192	$\beta = 107^\circ 55'$		109° 20'	(100) perfect. (001) imperfect.
4	$\text{PrEt}_2\text{NHgI}_2$	"	1.1350 : 1 : 0.7359	$\beta = 97^\circ 11'$		96° 48'	(110) perfect.
5	$\text{MePr}_2\text{NHgI}_2$	"	1.0749 : 1 : 0.6542	$\beta = 93^\circ 22'$		94° 2'	(011) fair. (110) imperfect.
6	$\text{EtPr}_2\text{NHgI}_2$	Rhombic	0.6890 : 1 : 0.5106	—		69° 8'	(011) perfect. (110) imperfect.
7	$\text{Pr}_2\text{NHgI}_2$	Monoclinic	1.4965 : 1 : 0.7328	$\beta = 113^\circ 16'$		107° 56'	(201) good.

\* The corresponding trimethylethyl and trimethylpropyl compounds were also prepared, but the crystals could not be obtained in a form suitable for measurement. In addition to the 1:1-compound, tetraethylammonium iodide also forms an orange-coloured substance with mercuric iodide in the molecular proportions 2:3. A description of this compound is included in the experimental part (p. 1314).



formula  $R_3\text{PhNHgI}_3$ , furnished clear cases of isomorphism. In the annexed table, the first member is not isomorphous with the succeeding compounds. The next three compounds, however, are clearly isomorphous, and, moreover, exhibit the following peculiarity. Although the compound  $\text{Me}_3\text{EtPhNHgI}_3$  (No. 9) differs from the compound  $\text{MeEt}_2\text{PhNHgI}_3$  (No. 11) by an amount expressible by  $\text{CH}_2$ , it is much more closely isomorphous with it than is the compound  $\text{Me}_3\text{PrPhNHgI}_3$  (No. 10), in spite of the fact that the last two compounds are isomerides. The similarity of angles between the first two mentioned compounds is, indeed, comparable with the close isomorphism met with in the sulphates of potassium, rubidium, caesium, and ammonium. The isomorphism of the three compounds numbered 9—11 was confirmed by a method which has been especially developed by one of us (T., 1906, 89, 1120). Crystal fragments of any one of the three substances continue to grow when placed in a saturated solution of either of the others, and thus satisfy one of the most rigid tests for isomorphism. Proceeding with the table, it is seen that there is a marked change of form in passing from No. 11 to No. 12, differing in composition by  $\text{CH}_2$ , but that the two compounds  $\text{Et}_3\text{PhNHgI}_3$  (No. 12) and  $\text{Et}_2\text{PrPhNHgI}_3$  (No. 13), also differing by  $\text{CH}_2$ , are closely isomorphous—a conclusion which was confirmed by the formation of regular growths when a crystal of one is immersed in a saturated solution of the other.

The choice of the final materials was, of course, dictated by practical considerations. Asymmetry of molecular configuration is most easily produced by the inclusion of a benzyl radicle, and the phenylbenzylalkylammonium group of compounds, represented by the general formula  $R_3(\text{CH}_2\text{Ph})\text{PhNHgI}_3$ , in which asymmetry is involved by the selection of different R-groups, was therefore examined. The results of the crystallographic examination are summarized in table III.

A glance at the values of the axial ratios is sufficient to show that the first substance has no really close relationship to the second and third compounds; moreover, the large discrepancy in the axial ratio  $b:c$  of the fourth substance shows that it also stands alone. The relationships of the second and third compounds (No. 15 and No. 16 of the table) deserve further notice. The axial ratios and angle  $\beta$  differ by relatively small amounts, thus indicating the possibility that the two substances are isomorphous. A comparison of the form-development points the same way. In the methylethyl derivative we have  $h\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $q\{011\}$ , and  $r\{201\}$ , with the forms  $b$  and  $a$  developed as small facets, whilst in the diethyl derivative we have

TABLE II.  
*The Phenylalkylammonium Group of Compounds.\**

No.	Substance.	System.	Crystallographic constants.		Prism angle.	Cleavage.
			$a : b : c.$	$\beta.$		
8	$\text{Me}_3\text{PhNHgI}_3$	Monoclinic	1.2400 : 1 : 0.6783	104°54'	100°18'	(100) good.
9	$\text{Me}_2\text{EtPhNHgI}_3$	"	0.7391 : 1 : 0.6783	94° 6'	72°48'	(001) perfect.
10	$\text{Me}_2\text{PrPhNHgI}_3$	"	0.7775 : 1 : 0.6711	90°34'	75°22'	(001) perfect.
11	$\text{MeEt}_2\text{PhNHgI}_3$	"	0.7319 : 1 : 0.6976	93°24'	72°18'	(001) perfect. (110) imperfect.
12	$\text{Et}_3\text{PhNHgI}_3$	"	1.1250 : 1 : 1.3490	101°21'	95°36'	(100) perfect.
13	$\text{Et}_2\text{PrPhNHgI}_3$	"	1.1185 : 1 : 1.3440	100°57'	95°22'	(100) perfect. (110) imperfect.

\* Phenyltriethylammonium iodide also forms a second type of compound with mercuric iodide in the molecular proportions 2 : 1. A description of this substance is included in the experimental part (p. 1318).

TABLE III.  
*The Phenylbenzylalkylammonium Group of Compounds.*

No.	Substance.	System.	Crystallographic constants.		Prism angle.	Cleavage.
			$a : b : c.$	$\beta.$		
14	$\text{Me}_3(\text{CH}_2\text{Ph})\text{PhNHgI}_3$	Monoclinic	0.7386 : 1 : 0.5105	93°26'	72°52'	(100) fair.
15	$\text{MeEt}(\text{CH}_2\text{Ph})\text{PhNHgI}_3$	"	0.9878 : 1 : 0.5797	106° 9'	87° 0'	(110) good.
16	$\text{Et}_2(\text{CH}_2\text{Ph})\text{PhNHgI}_3$	"	1.0301 : 1 : 0.6354	108° 7'	88°48'	(001) imperfect. (201) perfect.
17	$\text{MePr}(\text{CH}_2\text{Ph})\text{PhNHgI}_3$	"	1.1080 : 1 : 0.7768	102°55'	94°18'	(100).

the same forms, but without  $b(010)$  and  $a(100)$ . Since in the former compound these two forms were but slightly developed, their absence in the latter has no particular significance, merely indicating that one compound tends to present a richer form-development than the other. The coincidence of all the remaining forms, and, more especially, the occurrence in common of the form  $\{201\}$ , point to an identical space-lattice, and prove the substances to be isomorphous, in so far as purely geometrical characters can do so. This conclusion is strengthened by the observation that a broken fragment of the diethyl compound, when placed in a saturated solution of the methylethyl derivative, immediately begins to grow, and eventually becomes a perfect crystal.

The sole remaining question relates to the special chemical nature of phenylbenzylmethylethylammonium mercuri-iodide: whether the crystals are dextro- and levo-enantiomorphs, or are racemic or pseudo-racemic. As no trace of optical inhomogeneity was ever observed in crystals selected from various crops, and as the measurements gave no indications of the wide variations of angle characteristic of pseudo-racemic crystals, it follows that the crystals are either truly racemic or, on the other hand, a conglomerate of the two enantiomorphs. In order to decide this question, three of the largest crystals, weighing approximately 2, 1.5, and 1 gram respectively, were powdered, and as rapidly as possible dissolved separately in about 20 c.c. of acetone, and the solutions immediately examined in the polarimeter. In no case was an appreciable rotation observed; the crystals therefore presumably represent a true racemate. This conclusion was supported by etch-figures on the crystal faces, for they were in accordance with holohedral symmetry.

The main result of this investigation is to prove that racemic crystals of phenylbenzylmethylethylammonium mercuri-iodide are isomorphous with the corresponding diethyl derivative, although the racemic crystals contain two kinds of asymmetric molecules, whilst in the diethyl derivative all the molecules are necessarily identically similar and symmetrical.

#### EXPERIMENTAL.

##### *Preparation of Compounds.*

The general method of preparing the compounds was as follows. The proper molecular proportions of the tertiary amine, alkyl iodide, and mercuric iodide were warmed together with acetone until the whole was dissolved, and the solution allowed to remain overnight. Crystals were usually obtained the following day,

although two or three recrystallisations were sometimes necessary before really good crystals were formed.

Some of the compounds prepared were found to be unsuitable for crystallographic investigation; the trimethylethyl and trimethylpropyl compounds, for example, crystallise in needles. On the other hand, in some cases more than one compound is formed; thus, tetraethylammonium iodide unites with mercuric iodide in the proportions 1:1 and 2:3. With regard to the phenylalkyl group, it was observed that increase of molecular weight lowered the crystallisability of the compounds; sometimes five or six recrystallisations were necessary before sufficiently good crystals were obtained. The phenyldimethylpropyl and phenyldimethylethyl compounds have a strong tendency to form needles, but after repeated recrystallisations they finally yielded some measurable crystals. In one and the same solution, phenyltriethylammonium iodide forms with mercuric iodide two compounds, which on analysis proved to be the 2:1- and 1:1-compounds respectively; these were separated by hand. In the phenylbenzylalkyl group, the chemical combination of the various components was relatively slow; several attempts to prepare phenylbenzylethylpropylammonium mercuri-iodide were made, but a pure product could not be isolated.

#### *Method of Analysis.*

The method employed for the quantitative estimation of the mercury was that described by Marsh and Lye (*Analyst*, 1917, 42, 84). The process is a modification of the method of estimating mercury by combustion with quicklime. Calcium oxalate is placed at the closed end of the tube, and after this a few grams of dry calcium sulphate and quicklime; next comes about 1 gram of the substance ground up with about the same weight of potassium cyanide and a few grams of calcium sulphate and quicklime.\* After this, 5 or 6 grams of a mixture of calcium sulphate and quicklime are packed in, and the remainder of the tube is filled with quicklime. The vaporised mercury is collected in a small flask of water. No calcium sulphate was used with the tetramethyl, phenyldimethylpropyl, and phenyldiethylpropyl compounds. It may be noted that more satisfactory results were obtained with a tube longer than that recommended by Marsh and Lye; the length of the tube before drawing out should be about 50 cm.

\* In the case of the phenylbenzylalkylammonium group about a gram of black copper oxide was mixed with the substance and the potassium cyanide was placed nearer the drawn-out end of the tube.

*Method of Crystallographic Examination.*

A Fedorov two-circle goniometer was exclusively employed in the measurement of the crystals. Apart from its other advantages, a two-circle instrument is especially useful for the measurement of laboratory products, the crystals of which are frequently of microscopic dimensions, since it necessitates only one adjustment of the crystal. The results were plotted on a Fedorov stereographic net, and the crystal system, if not immediately obvious, was deduced from zonal angles, graphically determined by the help of the three-point compass and stereographic net, and later confirmed by an examination of the optical properties. The crystallographic indices were determined graphically in every case by the help of the gnomonic projection. In order to avoid possible errors, the axial ratios have been calculated in two independent ways for every compound. First, by the method in common use, depending on the solution of spherical triangles, and, secondly, by Goldschmidt's method (*Zeitsch. Kryst. Min.*, 1893, **21**, 210), based on the gnomonic projection. The crystal drawings were made directly from the gnomonic projection by the method devised by Goldschmidt (*Zeitsch. Kryst. Min.*, 1891, **19**, 352). Attention is especially called to this point, because the method does not appear to have come into general use, although experience proves it to be superior to all the other methods of drawing crystals.

In the descriptions of the crystals, the conventional rules have been adopted [in the monoclinic system, for instance, the indices (010) have been uniformly assigned to the plane of symmetry]; but, in addition, the "correct setting" of the crystal according to Fedorov's methods, and his "complex-symbol," have been worked out in every case, and the "transformation equations," by which the indices corresponding with Fedorov's theoretical ideas may be obtained from the conventional indices, are also given. The descriptions consequently contain everything necessary for an absolute identification of any of the compounds on any future occasion by the method now generally known as "crystallochemical analysis," a descriptive outline of which has already been given elsewhere (*Ann. Reports*, 1913, **10**, 245; 1914, **11**, 248; 1917, **14**, 227). An explanation of the meaning of the terms "transformation equations" and "complex-symbol" may well be appended here, as not having been previously given.

The connexion between the indices representing any face of a crystal when referred to two different sets of axes is most conveniently expressed by means of "transformation equations," by which one set of indices can be immediately deduced from the

other. Thus, in the case of the anorthic methyltriethylammonium mercuri-iodide (p. 1313), the new indices ( $pqr$ ) of any face referred to the axes chosen by Fedorov on structural grounds can be obtained from its indices ( $hkl$ ) when referred to the conventional axes by the equations:  $p = -1h + 0k + 2l$ ,  $q = 1h + 0k + 2l$ ,  $r = 1h + 2k + 0l$ . The numerical coefficients of  $hkl$  in these equations are 102, 102, and 120 respectively, and the equations can be abbreviated to "trans.  $\bar{1}02/102/120$ "—a form which is adopted in this paper.

The Fedorov "complex-symbol" is an expression which indicates simultaneously both the type of structural arrangement and the characteristic angles of the crystal (if necessary, after a suitable homogeneous deformation or shear). The initial term of the symbol is the number 6, 4, or 3, according as the crystal is held to approximate most closely to a hexagonal, tetragonal, or trigonal (rhombohedral) form respectively. When necessary, this number is immediately followed by a letter,  $h$ ,  $o$ , or  $d$ , respectively indicating, in Fedorov's phraseology, that the arrangement is "hexahedral" (that is, that of a simple space-lattice), "octahedral" (that of a centred lattice), or "dodecahedral" (that of a face-centred lattice). Thus  $4h$  signified that the type of the structural arrangement is that of a simple tetragonal space-lattice, whilst  $3d$  indicates the face-centred trigonal lattice as being the structural type. All remaining terms of the complex-symbol are numerical constants, representing degrees of arc, which serve to characterise each crystal species. As described below, one of these numerical terms, expressing in general the value of the angle (after a shear) between the correct basal plane and primary pyramid, is especially important in Fedorov's classification, so by way of contrast he encloses in brackets all other terms as are necessary to express the angular deviations of the lattice from an ideal hexagonal, tetragonal, or trigonal form. Thus, in the symbol " $(6)37\frac{1}{2}(+3)$ ," the first term means that the crystal approaches ideal hexagonal symmetry, the second that the principal angle is  $37\frac{1}{2}^\circ$ , and the third that the prism angle has the value  $60^\circ + 3^\circ$  instead of the value  $60^\circ$  proper to an ideal hexagonal lattice. The absence of any further term indicates that the system is orthorhombic. On the other hand, in the symbol " $(3h; +2)58(0)$ " we have a new kind of numerical term, namely,  $+2$ , immediately following the structural term  $3h$ . This means that the angle between two of the structural planes is not  $90^\circ$ , but  $90^\circ + 2^\circ$ , in other words, that the crystal is monoclinic with a value  $\beta = 92^\circ$ . The last term, " $(0)$ ," refers, as before, to the prism angle, and means that the deviation (from the ideal value of  $60^\circ$ ) is nearer

$0^\circ$  than  $\frac{1}{2}^\circ$ . The angles in the complex-symbols are only given to the nearest half degree, since this is the limit of accuracy of the graphical methods employed.

The Fedorov complex-symbol derives its immense importance from two facts: first, unlike axial ratios, it is an unambiguous constant for each crystal-species, and, secondly, such symbols can be readily classified in ordered form. In his "Dictionary of the Crystal-Kingdom," the publication of which by the Petrograd Academy of Science has been delayed by circumstances beyond its control, the late Professor Fedorov has classified all the existing data. All crystals belonging to the same type (say  $4h$  or  $3d$ , and so on) are first brought together, and then arranged in order according to the value of the principal angle mentioned above. Any well-developed crystalline substance which has once been measured, and placed in the dictionary in the place required by its complex-symbol, can be identified on any future occasion, for it is only necessary to measure the crystal to be identified, deduce its complex-symbol from the form-development, and refer to the dictionary for a statement of the chemical composition.

#### *Analytical and Crystallographic Details.*

Following is a detailed summary of the results of chemical analysis and crystallographic measurement of the various substances prepared. Although measured angles only are reproduced in this paper (the angles which served as a basis for calculation being marked with an asterisk), it may be mentioned that the correctness of the various indices was checked by the logarithmic computation of the angular values demanded by the law of simple, rational indices, and that these computed angles were in every case satisfactorily close to the measured angles. The omission of these computed angles results in a great saving of space and does not seem to us to involve the loss of anything essential to the future usefulness of the crystallographic descriptions.

*Tetramethylammonium Mercuri-iodide*,  $\text{Me}_4\text{NHgI}_3$ .—M. p. above  $200^\circ$  (Found:  $\text{Hg}=30.43$ . Calc.:  $\text{Hg}=30.53$  per cent.). Orthorhombic,  $a:b:c=0.5777:1:0.5199$ . Forms:  $b\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $n\{120\}$ ,  $c\{001\}$ ,  $e\{101\}$ ,  $p\{111\}$ ,  $t\{121\}$ . Two distinct habits were observed on crystals from acetone. The more usual habit is shown in Fig. 1. The second habit is bipyramidal and tabular parallel to  $b\{010\}$ . Following are the mean angular values obtained from five crystals:

	$b\{010\}$	$a\{100\}$	$m\{110\}$	$n\{120\}$	$c\{101\}$	$p\{111\}$	$t\{121\}$
Azimuth ( $\phi$ ) {.....}	$0^\circ 0'$	$90^\circ 4'$	$59^\circ 59'$	$40^\circ 50'$	$89^\circ 53'$	$59^\circ 59'$	$40^\circ 54'$
Polar distance, ( $\rho$ )	$89^\circ 59'$	$89^\circ 59'$	$90^\circ 0'$	$90^\circ 2'$	$41^\circ 59'$	$46^\circ 3'$	$53^\circ 57'$

Cleavages:  $a\{100\}$ , fair;  $c\{001\}$ , imperfect. Optic axial plane,  $a\{100\}$ ; acute bisectrix, perpendicular to  $\{001\}$ ; wide axial angle; birefringence, strong; dispersion  $\rho > v$ .

Trans.: 100/001/010. Complex-symbol,  $(4d)69(+3)$ .

*Methyltriethylammonium Mercuri-iodide*,  $\text{MeEt}_3\text{NHgI}_3$ .—M. p.  $104^\circ$  (Found:  $\text{Hg}=28.67$ .  $\text{C}_7\text{H}_{18}\text{NI}_3\text{HgI}_3$  requires  $\text{Hg}=28.73$  per cent.). Anorthic,  $a:b:c=1.1202:1.05578$ ;  $\alpha=102^\circ 55'$ ,  $\beta=95.6'$ ,  $\gamma=108^\circ 25'$ . Forms:  $b\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $n\{1\bar{1}0\}$ ,  $l\{2\bar{1}0\}$ ,  $q\{011\}$ ,  $t\{0\bar{1}1\}$ ,  $r\{101\}$ . The common habit is

FIG. 1.

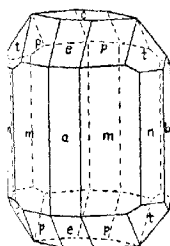
Tetramethylammonium  
mercuri-iodide.

FIG. 2.

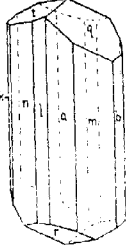
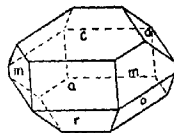
Methyltriethylammonium  
mercuri-iodide.

FIG. 3.

Tetraethylammonium  
mercuri-iodide.

slender prismatic, as shown in Fig. 2. Following are the mean angular values obtained from nine crystals:

	$b\{010\}$ .	$a\{100\}$ .	$m\{110\}$ .	$n\{1\bar{1}0\}$ .	$l\{2\bar{1}0\}$ .
Azimuth ( $\phi$ ) .....	$0^\circ 0'$	$70^\circ 5'$	$32^\circ 18'$	$130^\circ 40'$	$154^\circ 17'$
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$
	$l_2\{2\bar{1}0\}$ .	$q\{011\}$ .	$t\{0\bar{1}1\}$ .	$r\{101\}$ .	
Azimuth ( $\phi$ ) .....	$104^\circ 5'$	$4^\circ 29'$	$168^\circ 32'$	$281^\circ 43'$	
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$41^\circ 21'$	$19^\circ 3'$	$23^\circ 41'$	

Cleavages:  $m\{110\}$  and  $n\{1\bar{1}0\}$ , good. Optics: All the prism faces give oblique extinction.

Trans.:  $\bar{1}02/102/120$ . Complex-symbol,  $(4d; \pm 21)62(0; 0, ?)$ .

*Tetraethylammonium Mercuri-iodide*,  $\text{Et}_4\text{NHgI}_3$ .—M. p.  $110^\circ$  (Found:  $\text{Hg}=27.95$ . Calc.:  $\text{Hg}=28.13$  per cent.). Monoclinic,  $a:b:c=1.4826:1.08192$ ;  $\beta=107^\circ 55'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $r\{201\}$ ,  $o\{111\}$ . The common habit is stout prismatic, as shown in Fig. 3. Following are the mean angular values obtained from five crystals:

	$a\{100\}$ .	$m\{110\}$ .	$c\{001\}$ .	$r\{201\}$ .	$o\{111\}$ .
Azimuth ( $\phi$ ) .....	$90^\circ 0'$	$35^\circ 20'$	$89^\circ 46'$	$269^\circ 58'$	$342^\circ 34'$
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$90^\circ 0'$	$17^\circ 54'$	$39^\circ 56'$	$40^\circ 39'$

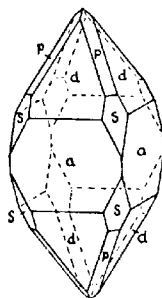


Cleavages:  $a\{100\}$ , perfect;  $c\{001\}$ , imperfect. Optic axial plane,  $b(010)$ . An optic axis emerges nearly perpendicular to  $c\{001\}$ .

Trans.:  $011/01\bar{1}/101$ . Complex-symbol,  $(4d; -14\frac{1}{2})55(-6\frac{1}{2})$ .

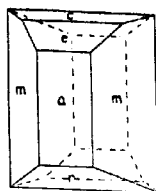
*Tetraethylammonium Mercuri-iodide*,  $2Et_4NI, 3HgI_2$ .—M. p.  $154^\circ$  (Found: Hg=31.94. Calc.: Hg=31.98 per cent.). Tetragonal,  $c:a=0.8186:1$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $e\{101\}$ ,  $d\{201\}$ ,  $p\{111\}$ ,  $s\{221\}$ . The common habit of the crystals is shown in Fig. 4. Following are the mean angular values obtained from four crystals:

FIG. 4.



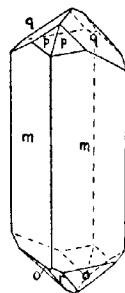
*Tetraethylammonium mercuri-iodide.*

FIG. 5.



*Triethylpropylammonium mercuri-iodide.*

FIG. 6.



*Methyltripropylammonium mercuri-iodide.*

	$a\{100\}$	$m\{110\}$	$c\{101\}$	$d\{201\}$	$p\{111\}$	$s\{221\}$
Azimuth ( $\phi$ ) .....	$0^\circ 0'$	$45^\circ 0'$	$0^\circ 3'$	$0^\circ 3'$	$45^\circ 3'$	$45^\circ 2'$
Polar distance ( $\rho$ ) .....	$90^\circ 0'$	$90^\circ 8'$	$39^\circ 13'$	$58^\circ 35'$	$49^\circ 9'$	$66^\circ 35'$

Cleavage:  $a\{100\}$ , good. Double refraction, very strong; positive. Complex-symbol,  $(4h)49^\circ 9'$ .

*Triethyl- $\alpha$ -propylammonium Mercuri-iodide*,  $Et_3PrNHgI_3$ .—M. p.  $85^\circ$  (Found: Hg=27.33.  $C_9H_{21}NI, HgI_2$  requires Hg=27.58 per cent.). Monoclinic,  $a:b:c=1.1350:1:0.7359$ ,  $\beta=97^\circ 11'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $e\{101\}$ ,  $r\{101\}$ ,  $p\{111\}$ . Two habits were observed, one of which is shown in Fig. 5. The second habit shows the pyramid  $p\{111\}$ , and  $a\{100\}$  is much narrower. Following are the mean angular values obtained from six crystals:

	$a\{100\}$	$m\{110\}$	$c\{001\}$	$e\{101\}$	$r\{101\}$	$p\{111\}$
Azimuth ( $\phi$ ) .....	$90^\circ 0'$	$41^\circ 36'$	$89^\circ 58'$	$89^\circ 59'$	$270^\circ 4'$	$46^\circ 39'$
Polar distance ( $\rho$ ) .....	$90^\circ 0'$	$90^\circ 0'$	$7^\circ 5'$	$37^\circ 51'$	$27^\circ 58'$	$46^\circ 59'$

Cleavage:  $m\{110\}$ , perfect. Optic axial plane,  $b(010)$ . An optic axis is visible through  $a\{100\}$  on the extreme edge of the field.

Trans.:  $\bar{1}10/\bar{1}\bar{1}0/002$ . Complex-symbol,  $(3h; +2)58(0)$ .

*Methyltri- $\alpha$ -propylammonium Mercuri-iodide*,  $\text{MePr}_3\text{NHgI}_3$ .—M. p.  $123^\circ$  (Found:  $\text{Hg} = 26.55$ .  $\text{C}_{10}\text{H}_{24}\text{NI}, \text{HgI}_2$  requires  $\text{Hg} = 27.06$  per cent.). Monoclinic,  $a:b:c = 1.0749:1.06542; \beta = 93^\circ 22'$ . Forms:  $m\{110\}$ ,  $q\{011\}$ ,  $r\{101\}$ ,  $p\{111\}$ ,  $o\{\bar{1}\bar{1}1\}$ . Two distinct habits were observed, one of which is shown by Fig. 6. The second habit is stout prismatic with large pyramidal faces. Following are the mean angular values obtained from five crystals:

	$m\{110\}$ .	$q\{011\}$ .	$r\{101\}$ .	$p\{111\}$ .	$o\{\bar{1}\bar{1}1\}$ .
Azimuth ( $\phi$ ) .....	$42^\circ 59'$	$4^\circ 59'$	$269^\circ 53'$	$45^\circ 37'$	$319^\circ 50'$
Polar distance ( $\rho$ ) ...	$90^\circ 1'$	$33^\circ 24'$	$28^\circ 56'$	$43^\circ 5'$	$40^\circ 26'$

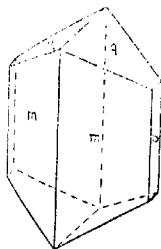
Cleavages:  $q\{011\}$ , fair;  $m\{110\}$ , imperfect. Optic axial plane,  $b(010)$ , and an optic axis is visible through  $a(100)$  on the edge of the field.

Trans.:  $110/\bar{1}\bar{1}0/002$ . Complex-symbol,  $(4o; +3\frac{1}{2})50(-2)$ .

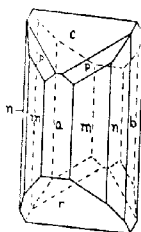
FIG. 7.

FIG. 8.

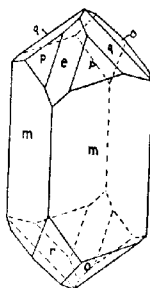
FIG. 9.



*Ethyltri- $\alpha$ -propylammonium mercuri-iodide.*



*Tetra- $\alpha$ -propylammonium mercuri-iodide.*



*Phenyltrimethylammonium mercuri-iodide.*

*Ethyltri- $\alpha$ -propylammonium Mercuri-iodide*,  $\text{EtPr}_3\text{NHgI}_3$ .—M. p.  $135^\circ$  (Found:  $\text{Hg} = 26.43$ .  $\text{C}_{11}\text{H}_{26}\text{NI}, \text{HgI}_2$  requires  $\text{Hg} = 26.56$  per cent.). Orthorhombic,  $a:b:c = 0.6890:1.05106$ . Forms:  $b\{010\}$ ,  $m\{110\}$ ,  $q\{011\}$ . The common habit is shown in Fig. 7. A second habit was observed much shortened along the vertical axis. Following are the mean angular values obtained from six crystals:

	$b\{010\}$ .	$m\{110\}$ .	$q\{011\}$ .
Azimuth ( $\phi$ ) .....	$0^\circ 0'$	$55^\circ 26'$	$0^\circ 0'$
Polar distance ( $\rho$ ) ...	$89^\circ 58'$	$90^\circ 0'$	$27^\circ 3'$

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Cleavages:  $q\{011\}$ , perfect;  $c\{001\}$ , imperfect. Optic axial plane,  $a\{100\}$ , and the  $c$ -axis is the negative acute bisectrix.

Trans.:  $100/011/002$  Complex-symbol,  $(6)37\frac{1}{2}(+3)$ .

*Tetra- $\alpha$ -propylammonium Mercuri-iodide*,  $\text{Pr}_4\text{NHgI}_3$ .—M. p.  $178^\circ$  (Found:  $\text{Hg}=25.75$ .  $\text{C}_{12}\text{H}_{28}\text{NI}, \text{HgI}_2$  requires  $\text{Hg}=26.07$  per cent.). Monoclinic,  $a:b:c=1.4965:1.07328$ ;  $\beta=113^\circ 16'$ . Forms:  $b\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $n\{120\}$ ,  $c\{001\}$ ,  $r\{201\}$ ,  $p\{111\}$ . The habit is prismatic, as shown in Fig. 8. Following are the mean angular values obtained from five crystals:

	$b\{010\}$ .	$a\{100\}$ .	$m\{110\}$ .	$n\{120\}$ .	$c\{001\}$ .
Azimuth ( $\phi$ ) .....	$0^\circ 0'$	$90^\circ 0'$	$*36^\circ 2'$	$20^\circ 1'$	$89^\circ 58'$
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$90^\circ 2'$	$90^\circ 2'$	$90^\circ 0'$	$*23^\circ 18'$

	$r\{201\}$ .	$p\{111\}$ .
Azimuth ( $\phi$ ) .....	$270^\circ 0'$	$52^\circ 45'$
Polar distance ( $\rho$ ) ...	$32^\circ 19'$	$*50^\circ 26'$

Cleavages:  $m\{110\}$  and  $r\{201\}$ , good. Optic axial plane  $b\{010\}$ . An optic axis emerges nearly perpendicular to  $r\{201\}$  and the acute negative bisectrix nearly coincides with the  $c$ -axis. Dispersion, moderate,  $\rho > v$ .

Trans.:  $011/011/101$ . Complex-symbol,  $(3d; -14)50(+1\frac{1}{2})$ .

*Phenyltrimethylammonium Mercuri-iodide*,  $\text{PhMe}_3\text{NHgI}_3$ .—M. p.  $135^\circ$  (Found:  $\text{Hg}=27.80$ .  $\text{C}_9\text{H}_{14}\text{NI}, \text{HgI}_2$  requires  $\text{Hg}=27.89$  per cent.). Monoclinic,  $a:b:c=1.2400:1.06783$ ;  $\beta=104^\circ 54'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $n\{210\}$ ,  $q\{011\}$ ,  $e\{101\}$ ,  $r\{301\}$ ,  $p\{111\}$ ,  $o\{111\}$ . The habit is prismatic, as shown in Fig. 9. Following are the mean angular values as obtained from five crystals:

	$a\{100\}$ .	$m\{110\}$ .	$n\{210\}$ .	$q\{011\}$ .	$e\{101\}$ .
Azimuth ( $\phi$ ) .....	$90^\circ 0'$	$*39^\circ 51'$	$59^\circ 6'$	$21^\circ 28'$	$90^\circ 0'$
Polar distance ( $\rho$ ) ...	$90^\circ 1'$	$90^\circ 0'$	$90^\circ 0'$	$36^\circ 6'$	$*39^\circ 46'$

	$r\{301\}$ .	$p\{111\}$ .	$o\{111\}$ .
Azimuth ( $\phi$ ) .....	$269^\circ 59'$	$50^\circ 54'$	$336^\circ 4'$
Polar distance ( $\rho$ ) ...	$55^\circ 7'$	$*47^\circ 2'$	$36^\circ 34'$

Cleavage:  $a\{100\}$ , good. Optic axial plane,  $b\{010\}$ . Through  $a\{100\}$  an optic axis is visible on the edge of the field.

Trans.:  $110/110/002$ . Complex-symbol,  $(4o; +15)48\frac{1}{2}(-5)$ .

*Phenyltrimethylethylammonium Mercuri-iodide*,  $\text{PhMe}_3\text{EtNHgI}_3$ .—M. p.  $95^\circ$  (Found:  $\text{Hg}=27.21$ .  $\text{C}_{10}\text{H}_{16}\text{NI}, \text{HgI}_2$  requires  $\text{Hg}=27.36$  per cent.). Monoclinic,  $a:b:c=0.7391:1.06783$ ;  $\beta=94^\circ 36'$ . The common habit is that of unmeasurable radiating needles. A few measurable crystals were obtained of the type shown in Fig. 10.

Forms:  $m\{110\}$ ,  $q\{011\}$ ,  $e\{101\}$ ,  $r\{\bar{1}01\}$ ,  $c\{001\}$ . Following are the mean angular values obtained from seven crystals (no trustworthy results were obtainable from the face  $c$ , which was always curved):

	$m\{110\}$ .	$q\{011\}$ .	$e\{101\}$ .	$r\{\bar{1}01\}$ .
Azimuth ( $\phi$ ) .....	$53^{\circ}36'$	$6^{\circ}2'$	$89^{\circ}59'$	$270^{\circ}0'$
Polar distance ( $\rho$ ) ...	$90^{\circ}1'$	$34^{\circ}18'$	$44^{\circ}43'$	$40^{\circ}22'$

Cleavage:  $c\{001\}$ , perfect. Optic axial plane,  $b(010)$ . An optic axis is visible through  $c\{001\}$  on the edge of the field. The dispersion of the optic axes is strong.

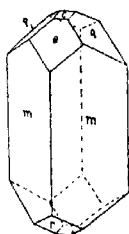
Trans.:  $\bar{1}01/\bar{1}01/010$ . Complex-symbol,  $(4d; 4)53(-2\frac{1}{2})$ .

*Phenyldimethyl- $\alpha$ -propylammonium Mercuri-iodide*,

$\text{PhMe}_2\text{Pr}\cdot\text{NHgI}_3$ .

—M. p.  $88^{\circ}$  (Found:  $\text{Hg}=26.54$ .  $\text{C}_{11}\text{H}_{15}\text{NI}, \text{HgI}_2$  requires  $\text{Hg}=26.84$  per cent.). Monoclinic,  $a:b:c=0.7775:1:0.6711$ ;  $\beta=96^{\circ}34'$ . Forms:  $m\{110\}$ ,  $q\{011\}$ ,  $e\{101\}$ ,  $r\{\bar{1}01\}$ . The common

FIG. 10.



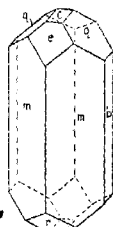
*Phenyldimethylethylammonium mercuri-iodide.*

FIG. 11.



*Phenyldimethylpropylammonium mercuri-iodide.*

FIG. 12.



*Phenyldimethyldiethylammonium mercuri-iodide.*

form is that of radiating needles. A few measurable crystals were obtained of the habit shown in Fig. 11, with prism faces much curved. Following are the mean angular values obtained from seven crystals:

	$m\{110\}$ .	$q\{011\}$ .	$e\{101\}$ .	$r\{\bar{1}01\}$ .
Azimuth ( $\phi$ ) .....	$53^{\circ}19'$	$9^{\circ}44'$	$89^{\circ}52'$	$269^{\circ}57'$
Polar distance ( $\rho$ ) ...	$90^{\circ}0'$	$34^{\circ}14'$	$44^{\circ}44'$	$38^{\circ}58'$

Cleavage:  $c\{001\}$ , perfect. Optic axial plane perpendicular to  $(010)$ . The acute negative bisectrix is nearly perpendicular to  $\{001\}$ . Dispersion strong,  $\rho > \nu$ .

Trans.:  $\bar{1}01/\bar{1}01/010$ . Complex-symbol,  $(4d; 6\frac{1}{2})52\frac{1}{2}(-4)$ .

*Phenyldimethyldiethylammonium Mercuri-iodide*,  $\text{PhMeEt}_2\text{NHgI}_3$ .

—M. p.  $96^{\circ}$  (Found:  $\text{Hg}=26.63$ .  $\text{C}_{11}\text{H}_{15}\text{NI}, \text{HgI}_2$  requires  $\text{Hg}=$

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26.84 per cent.). Monoclinic,  $a:b:c=0.7319:1:0.6976$ ;  $\beta=93^\circ 24'$ . Forms:  $b\{010\}$ ,  $m\{110\}$ ,  $n\{120\}$ ,  $c\{001\}$ ,  $q\{011\}$ ,  $e\{101\}$ ,  $r\{101\}$ . The common habit is shown by Fig. 12. Following are the mean angular values obtained from five crystals:

	$b\{010\}$ .	$m\{110\}$ .	$n\{120\}$ .	$c\{001\}$ .	$q\{011\}$ .
Azimuth ( $\phi$ ) .....	$0^\circ 0'$	$53^\circ 51'$	$34^\circ 18'$	$89^\circ 54'$	$4^\circ 52'$
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$3^\circ 25'$	$34^\circ 57'$

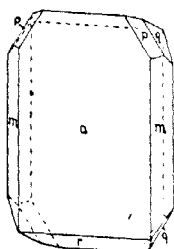
	$e\{101\}$ .	$r\{101\}$ .
Azimuth ( $\phi$ ) .....	$90^\circ 2'$	$269^\circ 57'$
Polar distance ( $\rho$ )	$45^\circ 19'$	$41^\circ 42'$

Cleavages:  $c\{001\}$ , perfect;  $m\{110\}$ , imperfect. Optic axial plane,  $b\{010\}$ . An optic axis is inclined at about  $20^\circ$  to  $c\{001\}$ . The double refraction is negative, with strong dispersion  $\rho < v$ .

Trans.:  $101/101/010$ . Complex-symbol,  $(4d; 3)55(+2)$ .

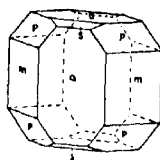
*Phenyltriethylammonium Mercuri-iodide*,  $\text{PhEt}_3\text{NHgI}_2$ .—M. p.  $98^\circ$  (Found:  $\text{Hg}=25.94$ .  $\text{C}_{12}\text{H}_{20}\text{NI}_2\text{HgI}_2$  requires  $\text{Hg}=26.35$  per

FIG. 13.



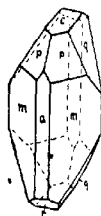
*Phenyltriethyl-  
ammonium mercuri-  
iodide (1:1).*

FIG. 14.



*Phenyltriethyl-  
ammonium mercuri-  
iodide (2:1).*

FIG. 15.



*Phenyltriethylpropyl-  
ammonium mercuri-  
iodide.*

cent.). Monoclinic,  $a:b:c=1.1250:1:1.3490$ ;  $\beta=101^\circ 20'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $r\{102\}$ ,  $q\{011\}$ ,  $p\{111\}$ . The common habit is shown by Fig. 13. Following are the mean angular values obtained from five crystals:

	$a\{100\}$ .	$m\{110\}$ .	$r\{102\}$ .	$q\{011\}$ .	$p\{111\}$ .
Azimuth ( $\phi$ ) .....	$90^\circ 0'$	$42^\circ 12'$	$269^\circ 58'$	$8^\circ 5'$	$46^\circ 33'$
Polar distance ( $\rho$ ) ...	$90^\circ 0'$	$90^\circ 1'$	$22^\circ 48'$	$53^\circ 39'$	$62^\circ 59'$

Cleavage:  $a\{100\}$ , perfect. Optic axial plane is  $b\{010\}$ . Inclined dispersion, strong.

Trans.:  $001/100/010$ . Complex-symbol,  $(4h; 9_4)46(-5_4)$ .

*Phenyltriethylammonium Mercuri-iodide*,  $2\text{PhEt}_3\text{NI}_2\text{HgI}_2$ .—M. p.  $144^\circ$  (Found:  $\text{Hg}=19.21$ .  $(\text{C}_{12}\text{H}_{20}\text{NI})_2\text{HgI}_2$  requires

Hg=18.80 per cent.). Orthorhombic,  $a:b:c=0.8642:1:1.1605$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $s\{104\}$ ,  $p\{111\}$ . The habit is shown by Fig. 14. Following are the mean angular values obtained from five crystals:

	$a\{100\}$ .	$m\{110\}$ .	$c\{001\}$ .	$s\{104\}$ .	$p\{111\}$ .
Azimuth ( $\phi$ ) .....	90° 0'	*49°19'	...	89°58'	49°16'
Polar distance ( $\rho$ ) ...	90° 0'	90° 0'	0° 0'	18°38'	*60°36'

Cleavage:  $c\{001\}$ , imperfect. Optic axial plane,  $b(010)$ ; the acute bisectrix is perpendicular to  $c\{001\}$ . The optic axial angle is wide.

Trans.: 010/100/001. Complex-symbol,  $(4d)60\frac{1}{2}(\pm 4)$ .

*Phenyldiethyl- $\alpha$ -propylammonium Mercuri-iodide*,

$\text{PhEt}_2\text{Pr}\cdot\text{NHgI}_3$ .

M. p. 93° (Found: Hg=26.33.  $\text{C}_{15}\text{H}_{22}\text{NI}\cdot\text{HgI}_3$  requires Hg=25.87 per cent.). Monoclinic,  $a:b:c=1.1185:1:1.3440$ ;  $\beta=100^\circ 57'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $q\{011\}$ ,  $r\{102\}$ ,  $p\{111\}$ . The common habit is shown by Fig. 15. Another habit was observed tabular to  $a\{100\}$ . Following are the mean angular values obtained from five crystals:

	$a\{100\}$ .	$m\{110\}$ .	$c\{001\}$ .	$q\{011\}$ .	$r\{102\}$ .	$p\{111\}$ .
Azimuth ( $\phi$ ) .....	90° 0'	*42°19'	90° 4'	8°10'	270°15'	*46°31'
Polar distance ( $\rho$ )	90° 1'	90° 1'	11° 0'	53°43'	22°45'	*62°53'

Cleavages:  $a\{100\}$ , perfect;  $m\{110\}$ , imperfect. Optic axial plane perpendicular to  $b(010)$ . The positive acute bisectrix is visible through  $a\{100\}$  on the edge of the field. Dispersion, strong,  $\rho < v$ .

Trans.: 001/100 010. Complex-symbol,  $(4h;11)50(\pm 6)$ .

*Phenylbenzylmethylammonium Mercuri-iodide*,

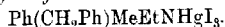
$\text{Ph}(\text{CH}_2\text{Ph})\text{Me}\cdot\text{NHgI}_3$ .

M. p. 143° (Found: Hg=24.74.  $\text{C}_{17}\text{H}_{19}\text{NI}\cdot\text{HgI}_3$  requires Hg=25.22 per cent.). Monoclinic,  $a:b:c=5.7386:1:0.5105$ ,  $\beta=92^\circ 26'$ . Forms:  $b\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $q\{011\}$ ,  $r\{101\}$ ,  $s\{121\}$ ,  $\phi\{141\}$ ,  $t\{321\}$ . The common habit is shown in Fig. 16. Following are the mean angular values obtained from five crystals:

	$b\{010\}$ .	$a\{100\}$ .	$m\{110\}$ .	$q\{011\}$ .	$r\{101\}$ .
Azimuth ( $\phi$ ) .....	0° 0'	89°59'	*53°34'	4°44'	270° 1'
Polar distance ( $\rho$ ) ...	90° 0'	90° 0'	90° 0'	27° 7'	32°57'
		$s\{121\}$ .	$\phi\{141\}$ .	$t\{321\}$ .	
Azimuth ( $\phi$ ) .....		*35°43'	342°24'	296°41'	
Polar distance ( $\rho$ ) ...		51°31'	65° 1'	66°15'	

Cleavage:  $a\{100\}$ , fair. Optic axial plane,  $b(010)$ .

Trans.: 010/101/103. Complex-symbol,  $(4d; -7\frac{1}{2})69(\pm 4)$ .

*Phenylbenzylmethylethylammonium Mercuri-iodide*,

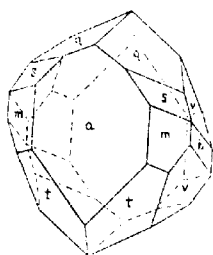
—M. p. 127° (Found: Hg = 24.68.  $\text{C}_{16}\text{H}_{30}\text{NI}_3\text{HgI}_2$  requires Hg = 24.78 per cent.). Monoclinic,  $a:b:c = 0.9878:1:0.5797$ ,  $\beta = 106^\circ 9'$ . Forms:  $b\{010\}$ ,  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $q\{011\}$ ,  $r\{201\}$ . The habit is shown in Fig. 17. Following are the mean angular values obtained from seven crystals:

	$b\{010\}$	$a\{100\}$	$m\{110\}$	$c\{001\}$	$q\{011\}$	$r\{201\}$
Azimuth ( $\phi$ )	0° 0'	90° 1'	*46°30'	90° 8'	26°37'	269°58'
Polar distance ( $\rho$ )	90° 0'	90° 0'	90° 0'	16° 9'	32°57'	42°51'

Cleavage:  $m\{110\}$ , good. Optic axial plane is  $b(010)$ . An optic axis is visible through  $r\{201\}$ . The dispersion is strong.

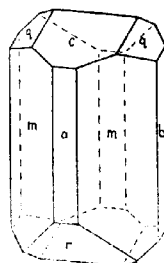
Trans.: 010/100/001. Complex-symbol,  $(4h; -16)40(1\frac{1}{2})$ .

FIG. 16.

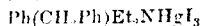


*Phenylbenzylmethylethylammonium mercuri-iodide.*

FIG. 17.



*Phenylbenzylmethylethylammonium mercuri-iodide.*

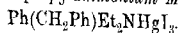
*Phenylbenzylmethylethylammonium Mercuri-iodide*,

—M. p. 138.5° (Found: Hg = 23.71.  $\text{C}_{17}\text{H}_{22}\text{NI}_3\text{HgI}_2$  requires Hg = 24.36 per cent.). Monoclinic,  $a:b:c = 1.0301:1:0.6354$ ,  $\beta = 108^\circ 7'$ . Forms:  $m\{110\}$ ,  $c\{001\}$ ,  $q\{011\}$ ,  $r\{201\}$ . The crystals are curved and distorted. The common habit is shown in Fig. 18. Following are the mean angular values obtained from seven crystals:

	$m\{110\}$	$c\{001\}$	$q\{011\}$	$r\{201\}$
Azimuth ( $\phi$ )	*45°36'	90° 0'	*27°14'	270° 0'
Polar distance ( $\rho$ )	90° 0'	18°25'	35°33'	43°49'

Cleavages:  $c\{001\}$ , imperfect;  $r\{201\}$ , perfect. Optic axial plane,  $b(010)$ , and there is an optic axis visible through  $r\{201\}$  on the edge of the field. There is strong dispersion.

Trans.: 010/100/001. Complex-symbol,  $(4h; -18)42(1\frac{1}{2})$ .

*Phenylbenzylmethyl- $\alpha$ -propylammonium Mercuri-iodide,*

—M. p.  $134^\circ$  (Found:  $\text{Hg} = 24.34$ .  $\text{C}_{17}\text{H}_{22}\text{NI}, \text{HgI}_2$  requires  $\text{Hg} = 24.36$  per cent.). Monoclinic,  $a:b:c = 1.1060:1.0:0.7766$ ,  $\beta = 102^\circ 55'$ . Forms:  $a\{100\}$ ,  $m\{110\}$ ,  $c\{001\}$ ,  $r\{101\}$ ,  $s\{221\}$ ,  $z\{221\}$ . The common habit is shown by Fig. 19. Following are the mean angular values obtained from seven crystals:

	$a\{100\}$ .	$m\{110\}$ .	$c\{001\}$ .	$r\{101\}$ .	$s\{221\}$ .	$z\{221\}$ .
Azimuth ( $\phi$ )	..... $90^\circ 0'$	$42^\circ 51'$	$89^\circ 52'$	$270^\circ 0'$	$47^\circ 4'$	$321^\circ 45'$
Polar distance ( $\rho$ )	$90^\circ 0'$	$90^\circ 0'$	$12^\circ 38'$	$26^\circ 45'$	$66^\circ 19'$	$63^\circ 1'$

FIG. 18.

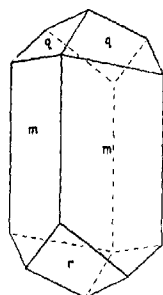
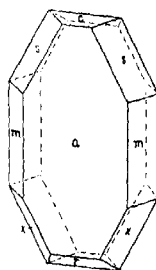
*Phenylbenzyl-diethylammonium mercuri-iodide.*

FIG. 19.

*Phenylbenzylmethylpropylammonium mercuri-iodide.*

Cleavage:  $a\{100\}$ . The optic axial plane is perpendicular to the plane of symmetry, and an optic axis is visible through  $m\{110\}$ .

Trans.:  $100\ 010\ 002$ . Complex-symbol,  $(4d; +13)64\frac{1}{2}(\pm 2)$ .

Our thanks are due to the Research Fund Committee of the Chemical Society and to the Scientific and Industrial Research Department for grants in aid of this work, and also to Professor H. L. Bowman, Mr. J. E. Marsh, and Professor W. H. Perkin for much help and advice.

MINERALOGICAL DEPARTMENT.

UNIVERSITY MUSEUM, OXFORD.

[Received, September 14th, 1920.]





## Organic Chemistry.

**Weight of a Normal Litre of Propane.** JEAN TIMMERMANS (*J. Chim. physique*, 1920, 18, 133--141).—Propane was prepared by the action of sodamide on propyl iodide (Lebeau, A., 1905, i, 401, 501) or by the action of sodium on butyronitrile (Stahrross, *J. Chim. physique*, 1912, 10, 497). The weight of a normal litre of the gas, prepared by either method, was found to be 2.0200 grams. W. G.

**Preparation of Propylene and its Homologues.** CHEMISCHE FABRIK BUCKAU (D.R.-P. 294794; from *Chem. Zentr.*, 1920, iv, 222).—A mixture of acetylene and its homologues with methane and its homologues is passed over a suitable non-metallic catalyst at 200—350°. The process may be carried out under increased pressure, or the mixture may be led through a contact apparatus completely filled with a porous catalyst. Titanic and silicic acids and their salts, as well as molybdic and tungstic acids, alumina, thorina, and zirconia, are recommended as catalysts. Examples are cited of the preparation of propylene from acetylene and methane, of butylene from acetylene and ethane, and of  $\Delta^2$ -butylene from allylene and methane. H. W.

**Conversion of Acetylene into Acetaldehyde and Acetic Acid.** B. NEUMANN and H. SCHNEIDER (*Zeitsch. angew. Chem.*, 1920, 33, 189--192).—For the conversion of acetylene into acetaldehyde on the laboratory scale, the best results were obtained by adding the gas, with vigorous mechanical stirring, into a catalyst composed of 96% acetic acid containing 3% of mercuric sulphate solution, the temperature being maintained at about 30°. Under these conditions, nearly 90% of the theoretical yield was obtained. At 40—50°, the rate of absorption was actually greater, but the percentage yield of acetaldehyde was reduced to 70—80. Using a dilute sulphuric acid medium instead of acetic acid, the reaction was more erratic, and, in favourable circumstances, only 70—75% yields were obtained. The optimum temperature in this case was 25—30°, and a very great decrease in the rate of absorption and increase in the formation of polymerised and resinous by-products was observed when the temperature was raised at all above this point. The best results in the direct conversion of acetylene into acetic acid were obtained by using the above mercuric sulphate-acetic acid catalyst with the addition of vanadium pentoxide, acetylene and oxygen being led in alternately. Yields of acetic acid up to 83% were obtained. G. F. M.

**Action of  $\alpha\beta$ -Chloroiodo-, Bromoiodo-, and Di-iodo-ethanes on the Sodium Sulphides.** MARCEL DELÉPINE and LUCIEN LILLE (*Bull. Soc. chim.*, 1920, [iv], 27, 678--679).—When sodium sulphide acts on  $\alpha\beta$ -chloroiodo-, bromoiodo-, or di-iodo-ethane in  
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aqueous or aqueous-alcoholic solution, ethylene, sulphur, and the sodium haloids are produced:  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{I} + \text{Na}_2\text{S} = \text{NaCl} + \text{NaI} + \text{S} + \text{C}_2\text{H}_4$ . A similar reaction occurs if sodium hydrogen sulphide is used in place of the neutral sulphide. W. G.

**Formation of Chlorohydrins. III.** L. SMITH and E. SAMUELSSON (*Zeitsch. physikal. Chem.*, 1920, **94**, 691—722. Compare A., 1918, i, 370).—The present paper deals with the formation of monochlorohydrin, and is divided into two portions; the first deals with the formation from glycerol and hydrogen chloride, whilst the second treats of the action of hydrogen chloride on glycide. In the first case, twenty-three syntheses have been effected, with yields varying from 10—70% of the monochlorohydrin. It is shown that the lower the temperature the greater the yield of the  $\alpha$ -chlorohydrin, and this is more noticeable if water is present from the beginning of the operation. Higher temperatures operate in the reverse way up to a certain point, which is probably to be explained by side reactions. In other words, the velocity with which hydrogen chloride attacks the secondary hydroxyl group has a greater temperature-coefficient than the velocity of the isomeric reaction. In the presence of succinic acid, and probably other catalysts, the  $\alpha$ -isomeride is the chief product, whilst water, which retards the reaction, increases the yield of the  $\beta$ -isomeride. The catalyses by raising the temperature and by succinic acid are therefore opposed to one another. At those temperatures where the  $\beta$ -isomeride is formed in appreciable quantity, it is also decomposed rapidly, and much more so than its isomeride. It is possible by the following method to obtain a 40% yield of the pure  $\alpha$ -isomeride: 0.5 gram-mol. of anhydrous glycerol containing 2 grams of succinic acid is treated with hydrogen chloride at  $18^\circ$  until there is an increase in weight of 18 grams. The addition of the hydrogen chloride takes place in two stages, with a pause of a day between the two additions. It is probable that a larger yield would be obtained if the mixture was kept longer. The unattached glycerol may be regained in probably quantitative yield by distillation. The highest yield of the  $\beta$ -isomeride obtained was 15%. The best laboratory method for the preparation of glyceryl  $\alpha$ -monochlorohydrin of approximate purity (1%  $\beta$ -isomeride) appears to be the following. Hydrogen chloride is passed into 1 gram-mol. of glycerol containing 4 grams of succinic acid until the weight has increased by 47 grams. The addition requires about eight hours, and the heat of the reaction keeps the temperature at  $60-70^\circ$ . The mixture should then be kept overnight. The yield in this case is 70%. If no special demands on the uniformity of the product are made, the reaction may be carried out at  $12^\circ$  until 39 grams of hydrogen chloride have been added. This gives a yield of 65%, and is much more conveniently carried out than the other methods.

The action of hydrogen chloride on glycide has been carried out in the following way: (i) leading hydrogen chloride into the pure glycide at  $-15^\circ$ ,  $100^\circ$ , and  $140-145^\circ$ ; (ii) leading hydrogen

chloride in ethereal solutions of the glycide at  $-76^{\circ}$ ,  $-15^{\circ}$ , and  $25-27^{\circ}$ ; (iii) dropping the glycide into (a) ethereal solutions of hydrogen chloride, (b) acetone solutions of hydrogen chloride, and (c) concentrated hydrochloric acid, at  $-76^{\circ}$ ,  $-14^{\circ}$ ,  $25-30^{\circ}$ ,  $50-55^{\circ}$ . The reaction velocity has been ascertained in each case. It is shown that at very low temperatures the chlorine enters the  $\alpha$ -position by preference, but the reaction is never simply this, some of the  $\beta$ -isomeride always being produced. J. F. S.

**Glyceryl  $\beta$ -Monochlorohydrin.** L. SMITH (*Zeitsch. physikal. Chem.*, 1920, **94**, 723-738. Compare preceding abstract).—After discussion of a number of methods for the preparation of glyceryl  $\beta$ -chlorohydrin, the author recommends the following method of procedure. A mixture of 97 grams of 95% glycerol and 150 grams of concentrated hydrochloric acid is heated for five hours at  $120^{\circ}$ . This is then distilled at a pressure of 15 mm., and the fraction distilling at  $110-150^{\circ}$  collected. This fraction is pure chlorohydrin, and contains 14-15% of the  $\beta$ -isomeride. The product is purified by a long-continued fractional distillation under reduced pressure. The following physical properties are recorded: boiling point,  $\alpha$ -isomeride,  $119-119.5^{\circ}/14.5$  mm.,  $\beta$ -isomeride,  $124.5-125^{\circ}/14.5$  mm.;  $\beta$ -isomeride,  $D^{20}_D$  1.3375,  $D^{20}_D$  1.3207;  $\alpha$ -isomeride,  $D^{20}_D$  1.3213. The molecular weight by the cryoscopic method in water solution is 113 (theory, 110.5). J. F. S.

**The History of Alcohol.** EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1920, **44**, 625. Compare A. 1913, i, 155, 244, 1298; 1918, , 210).—The recent publication of Sudhoff confirms the author's previous conclusion that the distillation of alcohol was first effected in connexion with that of rose-water and not, apparently, by the followers of any official medical school. Distilled alcohol does not appear to have been made before the middle of the twelfth century. H. W.

**Refractive Indices of Mixtures of isoPropyl Alcohol and Acetone.** DOROTHY MURIEL PALMER (*Analyst*, 1920, **45**, 302).—Tables are given showing the refractive indices of mixtures of acetone and isopropyl alcohol containing from 0 to 100% of the latter. W. P. S.

**Chloroformic Esters.** G. CAPELLI (*Gazzetta*, 1920, **50**, ii, 8-12).—In order to obtain chloroformic esters in good yield by the action of carbonyl chloride on an alcohol, the former reagent must always be present in considerable excess. Good results may be obtained by using furnace coke, which is carefully dried, broken into pieces the size of peas, cooled by means of pounded ice, and saturated with carbonyl chloride. The flow of the gas is subsequently increased and the alcohol added in rapid drops. In order that the whole of the alcohol may be converted into ester and that the excess of carbonyl chloride may escape, the crude ester is left in a strong draught for about twenty hours, and is then

washed with ice-water, dried by means of calcium chloride, and fractionally distilled. The use of basic substances is unnecessary and the alcohol need not be anhydrous, 90% yields being obtained from alcohol of 76% concentration.

T. H. P.

**Improvements in Methods of Forming Esters.** U.S. INDUSTRIAL ALCOHOL Co. (Brit. Pat. 147337).—Esters of the higher alcohols are produced by partial esterification in presence of a dehydrating agent, separating the latter, and continuing the esterification at a higher temperature. For instance, a mixture of 3205 grams of fusel oil (D 0.8268), 256 grams of concentrated sulphuric acid, and 2564 grams of glacial acetic acid is kept for twenty-four hours at the ordinary temperature with occasional agitation. The aqueous layer containing all the sulphuric acid is separated, and the oily layer distilled at 100° until no further separation of water occurs, indicating that esterification has ceased. The oily layer in the distillate is from time to time separated from the water and returned to the still, the contents of which are finally neutralised with 30% sodium hydroxide solution. The sodium acetate layer which separates is drawn off and distilled at 100° to recover any amyl acetate it may contain.

G. F. M.

**Anomalies in the Solidification Point of Tristearin.** BEN H. NICOLET (*J. Ind. Eng. Chem.*, 1920, **12**, 741—743).—The double melting point of tristearin is attributed to the existence of two modifications, the more stable of which has m. p. 71.6—72.2°, and the unstable form about 55°, the latter being reconverted into the stable form on heating it at a higher temperature or allowing it to remain. In spite of the speed of solidification, the solidification point of tristearin is usually given as that of the unstable form (about 55°). The solidification point of pure tristearin was determined by the rise of temperature in Dalcian's method. It first showed signs of solidification at 53.8°; the temperature then rose normally to about 63.5°, remained almost constant for some time, and then rose rapidly to the maximum at about 69°. On "seeding" liquid tristearin with the stable modification above 60°, solidification takes place without the formation of the unstable form, but the latter is apparently always produced after seeding, even with the stable form, at temperature below 56°. Double solidification points are not necessarily shown by all the triglycerides which show a double melting point. It appears to be an essential condition that the solidification of the unstable form shall produce sufficient heat to reach the temperature of transition into the stable form. The phenomenon was shown by hydrogenated soya bean oil, but not by hydrogenated linseed or cotton-seed oil. The solidification point of hydrogenated linseed oil (65.9°) was not raised by "seeding."

C. A. M.

**Fat Associated with Starch.** T. C. TAYLOR and J. M. NELSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1726—1738).—Corn starch, carefully freed from adherent or associated fat by repeated extraction

with ether, light petroleum, and carbon tetrachloride, gave on hydrolysis a material from which fat or free fatty acids could be extracted. The principal constituent of this "fat by hydrolysis" was palmitic acid, but there was, in addition, an unsaturated compound of unknown constitution. By controlled acid hydrolysis it was found that this fat was liberated when the hydrolysis had reached the erythro-dextrin stage. Fat is also obtained by diastatic hydrolysis or hydrolysis with *Bacillus aceto-ethylicum*. By controlling the hydrolysis of the starch, it is possible to obtain residues containing relatively large amounts of fat combined with carbohydrate. Analytical data indicate that the palmitic acid is probably attached directly to the unsaturated compound mentioned above in the form of an ester. Starches from other vegetable sources also contained varying amounts of "fat by hydrolysis," the amounts obtained varying from 0.04--0.83%.

W. G.

**Photochemical Chlorination of Methyl Sulphate. Preparation of Chloromethyl Sulphate.** VOLMAR (*Bull. Soc. chim.*, 1920, [iv], 27, 681--684).—Methyl sulphate readily undergoes chlorination at the ordinary temperature under the influence of ultra-violet rays, and more slowly under the influence of the light from an arc lamp or a metal filament lamp. The product is, in all cases, methyl chloromethyl sulphate,  $\text{CH}_3\text{Cl} \cdot \text{MeSO}_4$ . The fixation of a second chlorine atom is not possible, because it requires radiations of such a wave-length that the dichloromethyl sulphate is decomposed as it is formed.

W. G.

**Catalytic Oxidation by Unsaturated Compounds (Oils, Hydrocarbons, etc.).** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1920, 171, 353--355).—When a solution of  $\beta\beta'$ -dichlorodiethyl sulphide in turpentine is exposed to air, the sulphide undergoes oxidation, giving  $\beta\beta'$ -dichlorodiethyl sulphoxide,  $\text{SO}(\text{C}_2\text{H}_4\text{Cl})_2$ , m. p. 112°, which, when oxidised with potassium permanganate in acid solution, gives  $\beta\beta'$ -dichlorodiethylsulphone,  $\text{SO}_2(\text{C}_2\text{H}_4\text{Cl})_2$ , m. p. 55°, and when treated with aqueous potassium hydroxide gives  $\beta\beta'$ -dihydroxydiethyl sulphoxide,  $\text{SO}(\text{C}_2\text{H}_4\text{OH})_2$ , m. p. 111°. The turpentine may be replaced by various unsaturated oils and hydrocarbons. Similarly, when  $\beta\beta'$ -dihydroxydiethyl sulphide in solution in citraldehyde is exposed to air, it gives the dihydroxydiethyl sulphoxide described above.

That these oxidations are due to the catalytic action of the unsaturated solvents is shown by the fact that  $\beta\beta'$ -dichlorodiethyl sulphide in the pure state or in solution in a saturated oil does not undergo oxidation when exposed to air.

W. G.

**Triethylene Tri- and Tetra-sulphides.** (Sir) PRAFULLA CHANDRA RAY (*T.*, 1920, 117, 1090--1092).

**Optical Rotation of Dextrose under the Influence of Hydrochloric or Sulphuric Acid.** I. HANS MÜRSCHHAUSER (*Biochem. Zeitsch.*, 1920, 104, 214--236).—Experiments with

hydrochloric acid at the ordinary temperature indicate that the influence of acid on the mutarotation of dextrose consists in an acceleration of the reaction to an extent increasing with the concentration of the acid; the accelerating effect of sulphuric acid is less than that of hydrochloric acid. The value of the final specific rotation increases with the proportion of acid present in the solution. Especially when the acidity is low, the rotation of dilute dextrose solutions is affected by hydrochloric acid less than that of more concentrated solutions. With the 10% acid, the specific rotation remains constant for a long time independently of the concentration; with the 20% acid, the rotation of dilute dextrose solutions does not change over a long period, but that of the more concentrated solutions gradually rises; 30% of hydrochloric acid produces a permanent increase in the rotation, this being greater for the high than for the low concentrations; 46% of the acid causes an initial increase in the rotation for the higher concentrations of the sugar, but continuous fall in the rotation soon begins, owing to decomposition of the dextrose.

T. H. P.

**Action of the Carbonates of the Alkaline Earths on Dextrose. II. Dextrose and Calcium Carbonate.** HANS MÜRSCHHAUSER (*Biochem. Zeitsch.*, 1919, **99**, 190—204).—The modified dextrose obtained by boiling a solution of dextrose with calcium carbonate for three hours (this vol., i, 13) is fermentable. The presence of levulose in it was demonstrated by Selivanov's reaction and by the separation of levulose phenylmethyllosazone by Neuberg's method.

S. S. Z.

**Dry Distillation in a Vacuum and its Application to the Study of Carbohydrates.** AMÉ PICTET (*Bull. Soc. chim.*, 1920, [iv], **27**, 641—656).—A lecture delivered before the French Chemical Society.

**The Ethylene-oxide Structure of Sucrose and some other Carbohydrates.** EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH (*T.*, 1920, **117**, 1086—1090).

**Cellulose Acetate.** H. J. H. FENTON and A. J. BERRY (*Proc. Camb. Phil. Soc.*, 1920, **20**, 16—22).—The work described was mainly on the lines of investigating (a) substitutes for acetone as a solvent; (b) the influence of the mode of preparation on the properties of the product; (c) the characterisation and analysis of cellulose acetate.

No general conclusion can be drawn as regards the chemical nature of a liquid and its solvent action on cellulose acetate, although there appears to be some relation between the dielectric constant and solvent action. The authors consider that in Miles's method for the conversion of the cellulose acetate from an insoluble to an acetone-soluble form, partial hydrolysis, and not hydration, occurs. For the estimation of the acetyl group, the authors prefer Ost's method of cold alkaline hydrolysis (*A.*, 1912, i, 680).

W. G.

**The Supposed Degradation of Starch by means of Formaldehyde.** J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, 99, 316—320).—A final reply to Woker's criticism (this vol., i, 689).  
S. S. Z.

**Iron Salt of Carbohydrate-Phosphoric Acid.** KARL SCHWEIZER (*Bull. Assoc. chim. Sucr.*, 1920, 37, 464—468).—See this vol., i, 531.

**Synthesis of Phytic Acid.** R. J. ANDERSON (*J. Biol. Chem.*, 1920, 43, 117—128).—The reaction between inositol, phosphoric acid, and phosphoric oxide has been again studied (compare Posternak, A., 1919, i, 433). The main product of this reaction appears to be an inositol ester of pyrophosphoric acid containing 4 atoms of phosphorus or 2 mols. of pyrophosphoric acid, and corresponding with the formula  $C_6H_{12}O_{16}P_4$ . This does not agree with the conclusion reached by Posternak (*loc. cit.*), who believed the chief product to be identical with the natural phytic acid or inositol-hexaphosphoric acid,  $C_6H_{12}O_{16}P_6$ .  
J. C. D.

**Complex Metallic Ammines. IV. *cis*-Sulphoacetato-, *cis*-Methionato-, and *cis*-Dimethylmalonato-diethylenediaminecobaltic Salts.** THOMAS SLATER PRICE and JAMES COOPER DUFF (T., 1920, 117, 1671—1677).

**ψ-Muscarine ("Synthetic Muscarine").** ALBERT B. WEINHAGEN (*J. Amer. Chem. Soc.*, 1920, 42, 1670—1678).—The action of nitric acid on choline platinichloride, according to the original directions of Schmiedeberg and Harnack (*Arch. exp. Path. Pharm.*, 1877, 6, 101), gives as the principal product the platinichloride of choline nitrite (compare Ewins, A., 1914, i, 665), and in addition a compound, m. p. 204—205°, which is probably dimethylaminoethyl nitrate platinichloride and trimethylamine platinichloride. By deviating from the original directions by evaporating five times with nitric acid instead of only once, choline nitrite was not obtained, the main products being trimethylamine platinichloride and a compound, m. p. 208°, probably having the constitution  $[NMe_3CH_2CH(OH)_2]PtCl_3$ , assigned by Schmiedeberg and Harnack (*loc. cit.*) to "synthetic muscarine." In addition to the platinichloride, the derivatives of choline nitrite obtained were the *hydrochloride*, m. p. 165°, the *aurichloride*, the *sulphate*, the *perchlorate*, and the *free base*.

The pharmacological effects of "synthetic muscarine" reported by different observers must be considered with the above facts in mind.  
W. G.

**Manufacture of Complex Silver Salts of Aliphatic α-Amino-acids.** HERMANN RICHARD NAFF (*Brit. Pat.* 148074).—Complex silver salts of aliphatic α-amino-acids are obtained by dissolving freshly precipitated silver oxide, or organic or inorganic salts of silver, in a solution containing an excess of the amino acid



and allowing to crystallise, after suitable evaporation, if necessary, except in the case of the glycine compound, where crystallisation must be effected at temperatures below  $0^{\circ}$ , or otherwise the normal silver salt is obtained. These complex salts are more stable and more readily soluble in water than the normal salts, and do not give all the reactions of the silver cation, sodium hydroxide or carbonate, for instance, giving no immediate precipitation. The aqueous solutions are alkaline to litmus and do not precipitate albumin. The compounds have no irritating effect, and this, together with their other properties, renders them suitable for therapeutic purposes. G. F. M.

#### Decomposition of Glutamic Acid and its Salts on Heating.

VLAD ŠKOLA (*Zeitsch. Zuckerind. Cechoslov.*, 1920, **44**, 347—351, 355—360, 363—368, 370—374).—Glutamic acid melts at  $211^{\circ}$  when very rapidly heated; when heated more slowly, or after prolonged drying at  $110^{\circ}$ , it shows a lower m. p., owing to slight decomposition (compare Menozzi and Appiani, A., 1894, i, 498). The conversion of *D*-glutamic acid into its lactam, *L*-glutimic acid (Stanik, A., 1912, i, 952), probably takes place to a slight extent when the former is simply dissolved in water. Equilibrium is attained in 2% solution after boiling for 100 hours, and 90–95% of glutimic acid is formed. The reaction is unimolecular. In presence of sulphuric or hydrochloric acid, the equilibrium is displaced in favour of glutamic acid; the displacement is a function of the concentration of mineral acid, and is much greater with hydrochloric than with sulphuric acid at the same concentration. Glutimic acid found in products of protein hydrolysis may thus be a secondary product only, and its amount may vary according as sulphuric or hydrochloric acid was used as hydrolyst. The pyrrolidone-2-carboxylic acid formula for glutimic acid is confirmed by the author's observation that this acid does not react with formaldehyde by Sørensen's method. The nitrogen of glutamic acid, on the other hand, reacts almost quantitatively provided that successive additions of formaldehyde are made alternating with neutralisation of the acidity developed by each addition. [See also *J. Soc. Chem. Ind.*, 1920, Oct.] J. H. L.

#### Synthesis of a Second Diamide, Oxamide, by Oxidation of Sucrose and Ammonia.

R. FOSSE (*Compt. rend.*, 1920, 171, 398—400).—When a solution of sucrose in strong ammonium hydroxide is oxidised by calcium permanganate, oxamide is obtained, and the course of the reaction is considered to be  $2C_6H_{12}O \rightarrow 2HCN \rightarrow (CN)_2 \rightarrow (CO \cdot NH)_2$ . W. G.

**The Constitution of Carbamides. XI. The Mechanism of the Synthesis of Urea from Ammonium Carbamate. The Preparation of certain Mixed Tri-substituted Carbamates and Dithiocarbamates.** EMIL ALPHONSE WERNER (*L.* 1920, 117, 1046—1053).

**The Constitution of Carbamides. XII. The Decomposition of Urea when Heated in Solution in the Presence of Acids.** EMIL ALPHONSE WERNER (T., 1920, 117, 1078—1081).

**The Nature of the  $\beta$ -Ferricyanides and the  $\beta$ -Ferrocyanides.** SAMUEL HENRY CLIFFORD BRIGGS (T., 1920, 117, 1026—1034).

**Estimation of Active Hydrogen in Organic Compounds.**

R. CIUSA (*Gazzetta*, 1920, 50, ii, 53—55).—The method suggested by Moureu and Mignonac for diagnosing amines by treating them with magnesium ethyl bromide in ethereal solution and measuring the volume of ethane formed (A., 1914, i, 808) was first suggested by Tschugaev (A., 1903, i, 79) for the determination of the atoms of active hydrogen.

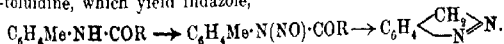
The author applies Moureu and Mignonac's experimental conditions to methyl alcohol, phenol, resorcinol,  $\alpha$ -naphthol, pyrrole, 2-methylindole, phenylbenzylidenehydrazine, ethyl acetoacetate and ethyl ethylacetoacetate, nitromethane and nitroethane, the values obtained for the number of atoms of active hydrogen being either those required or in agreement with the results of previous investigators. 1-Methylpyrrole, 1-methylindole, and trinitrobenzene yielded no gas.

T. H. P.

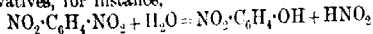
**Reactions of certain Ortho- and Para-substituted Benzene Derivatives.** A. ANGELI (*Gazzetta*, 1920, 50, ii, 1—8; *Atti R. Accad. Lincei*, 1920, [v], 29, i, 375—381).—The author has shown previously (A., 1917, i, 452) that hydrogen peroxide, hydroxylamine, and hydrazine exhibit chemical analogy to quinol, *p*-aminophenol, and *p*-phenylenediamine, and that in some reactions of ortho- and para-substituted aromatic compounds, the two substituent groups behave as though directly joined. Further examples of such analogy are now given.

The reaction between a ketone and ethyl oxalate,  $R \cdot CO \cdot Me + (CO_2Et)_2 \rightarrow R \cdot CO \cdot CH_2 \cdot CO \cdot CO_2H$ , is quite analogous to that between *o*- or *p*-nitrotoluene and the ester,  $C_6H_4Me \cdot NO_2 + (CO_2Et)_2 \rightarrow NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO_2H$ . With the aliphatic compounds, it is the negative group (CO, CN, etc.) which impresses increased mobility on the hydrogen atoms of the methyl group, whereas with the aromatic compounds this purpose is served by the nitro-group, which enhances the negative character of the whole of the aromatic residue.

The hydrolysis of certain methylamine derivatives, with formation of diazomethane,  $NHMe \cdot COR \rightarrow NO \cdot NMe \cdot COR \rightarrow CH_2N_2$ , is similar to the behaviour of analogous derivatives of *o*-toluidine, which yield indazole,

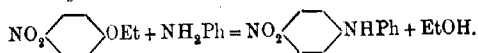


The transformations produced in certain *o*- and *p*-substituted nitro-derivatives, for instance,



c c

and  $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{Cl} + \text{H}_2\text{O} = \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{HCl}$ , correspond with those exhibited by  $\text{N}_2\text{O}_4$  and  $\text{NO}_2\text{Cl}$ . Further, the formation of phenylnitroamine from ethyl nitrate and aniline,  $\text{NO}_2\cdot\text{OEt} + \text{NH}_2\text{Ph} = \text{NO}_2\cdot\text{NHPh} + \text{EtOH}$ , is analogous to the reaction



Another group of transformations indicating the connexion between two ortho- or para-substituents is that in which one or both of the oxygen atoms of a nitro-group migrate to a carbon atom. Among these are (1) the formation of *p*-aminobenzaldehyde by the action of alkali sulphide on *p*-nitrotoluene, (2) the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid under the influence of light, (3) the transformation of *o*-nitrotoluene into *o*-nitrosobenzyl alcohol, and (4) that of *o*-nitrotoluene into anthranilic acid by the action of an alkali. Owing to the marked alterability of the aromatic hydroxylamines and the different behaviour of aliphatic aldehydes and nitro-derivatives, it is not always possible to realise the analogous transformations in the two series, but nitromethane, for instance, readily undergoes the following changes:  $\text{NO}_2\text{Me} \rightarrow \text{OH}\cdot\text{NH}\cdot\text{CHO} \rightarrow \text{NH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{NH}_3 + \text{CO}_2$ .

A parallel to the oxidation of aliphatic nitro-derivatives,  $2\text{NO}_2\cdot\text{CHR}\cdot\text{CHR}\cdot\text{NO}_2 \rightarrow \text{NO}_2\cdot\text{CHR}\cdot\text{CHR}\cdot\text{NO}_2$ , is found with *o*- and *p*-nitrotoluenes, which undergo a similar change without oxidising agents, the oxidation being effected by part of the nitro-compound itself,  $2\text{NO}_2\cdot\text{C}_6\text{H}_4\text{Me} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . In the case of nitromethane, another product, metazonic acid, containing one oxygen atom less, is also obtained.

Analogies also appear between the physiological behaviour of certain corresponding derivatives of the aliphatic and aromatic series. Thus, ethylurethane exerts a hypnotic action, whereas ethyl *p*-aminobenzoate acts as an anæsthetic. Further, hydrazine is poisonous, as also is *p*-phenylenediamine. Aliphatic diamines, such as putrescine and cadaverine, are, however, physiologically inert, and the conclusion is drawn that the same holds for 1:4-diaminocyclohexane.

T. H. P.

**Preparation of Picryl Chloride by Nitration of 4 Chloro-1:3-dinitrobenzene.** PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER (*J. Soc. Chem. Ind.*, 1920, **39**, 257-260).—For the preparation of picryl chloride from chlorodinitrobenzene, it is recommended to use 100 grams of chlorodinitrobenzene, 750 grams of 100% sulphuric acid, and 125 grams of 90% nitric acid, the nitration being conducted at 130° for twelve hours. If 96% sulphuric acid is used, the amount must be doubled and the amount of nitric acid increased to 175 grams. A portion of the chlorodinitrobenzene is oxidised, the ratio of the amount of nitric acid used in nitration to the amount used in oxidation being 1:1.8.

W. G.

**Organic Molecular Compounds. IV. Addition of Alkyloxy- to the Nitro-group.** M. GIUA and A. MARCELLINO

(*Gazzetta*, 1920, 50, i, 341—359. Compare A., 1916, i, 205).—In order to ascertain if the property of forming more or less intensely coloured additive compounds with polynitro-derivatives exhibited by aromatic compounds containing a phenolic hydroxyl group persists when the hydroxyl is etherified, the authors have investigated cryoscopically the binary systems formed by *m*-dinitrobenzene, 2:4-dinitrotoluene, 2:4:6-trinitrotoluene, and picric acid with  $\beta$ -naphthol methyl ether and the dimethyl ether of quinol.

The results obtained show that 2:4:6-trinitrotoluene and picric acid, but not *m*-dinitrobenzene or 2:4-dinitrotoluene, form compounds with the ethers mentioned. With the exception of that formed from the dimethyl ether of quinol and picric acid, the nature of the additive compound does not depend on the number of alkyloxy-groups present. Further, the presence of the double ring in  $\beta$ -naphthol is without influence on the formation or non-formation of the additive compound, this observation being in agreement with Sudborough's conclusion that, as regards the property of forming additive compounds, a condensed system of two or more benzene rings may be considered as a single ring (T., 1916, 109, 1339).

The molecular compounds which 2:4:6-trinitrotoluene and picric acid form with  $\beta$ -naphthol methyl ether and the dimethyl ether of quinol show intense coloration varying from pale yellow to orange-yellow. As in certain similar cases, the colour of the compound is related to the auxochrome group, but for the formation of the compound and of the colour the presence of three nitro-groups in one of the two components is a necessary condition. Which of the three nitro-groups is added to the alkyloxy-group has not yet been established, but from Werner's conception that mutual saturation of the secondary valencies of the chromophore and auxochrome groups must be assumed in the molecular compounds (A., 1910, i, 20), it seems probable that the additive compounds now described are formed by means of the valencies between the characteristic functional groupings; the influence of the aromatic nucleus must not, however, be overlooked. These results are discussed in relation to those obtained by Giua and Cherchi (this vol., i, 303).

The system *m*-dinitrobenzene: $\beta$ -naphthol methyl ether forms a single eutectic, m. p. about 42°, containing 50% by weight of the nitro-compound. 2:4-Dinitrotoluene: $\beta$ -naphthol methyl ether, one eutectic, m. p. about 34°, 57% of nitro-compound. 2:4:6-Trinitrotoluene: $\beta$ -naphthol methyl ether forms a compound, m. p. about 73°, containing 1 mol. of each component; the eutectic between the compound and the trinitrotoluene has m. p. about 60°, and that between the compound and the ether m. p. 58°. Picric acid (1 mol.) and  $\beta$ -naphthol methyl ether (1 mol.) form a compound, m. p. about 114°, the eutectics between this compound and the picric acid and ether melting at 99° and 67.4°

respectively. *m*-Dinitrobenzene:dimethyl ether of quinol gives a single eutectic, m. p. about  $30^{\circ}$ , at a concentration of 50%. 2:4-Dinitrotoluene:dimethyl ether of quinol forms one eutectic, m. p. about  $30^{\circ}$ , at a concentration of 50%. 2:4:6-Trinitrotoluene (1 mol.) and the dimethyl ether of quinol (1 mol.) form a compound, m. p.  $43.3^{\circ}$ , the eutectics between this compound and the nitro-compound and ether melting at  $42.2^{\circ}$  and about  $38^{\circ}$  respectively. Picric acid (2 mols.) and the dimethyl ether of quinol (3 mols.) form a compound which has an indistinct melting point and dissociates on melting. *m*-Dinitrobenzene (1 mol.) and  $\beta$ -naphthol (1 mol.) give a compound, m. p. about  $62^{\circ}$  (dissociating). 2:4-Dinitrotoluene (1 mol.) and  $\beta$ -naphthol (1 mol.) form a compound, m. p.  $76.6^{\circ}$ , the eutectics between this compound and the components melting at about  $59^{\circ}$  and about  $74^{\circ}$  respectively. 2:4:6-Trinitrotoluene (1 mol.) and  $\beta$ -naphthol (1 mol.) give a compound, m. p.  $109.4^{\circ}$ , the eutectics between this compound and the components melting at  $73.5^{\circ}$  and  $97.5^{\circ}$  respectively.

The fused mixtures of the nitro-compounds examined with the ethers of  $\beta$ -naphthol and quinol and with  $\beta$ -naphthol are all more or less intense yellowish-red. Only for the systems in which a single eutectic appears are the mixtures pale yellow in the hot and almost colourless when cold.

T. H. P.

**4-Nitro-*o*-toluenesulphonic Acid.** S. V. HINTIKKA (Can. Pat. 200291).—This acid is prepared by sulphonating *p*-cymene to its *o*-sulphonic acid and treating the sulphonation mixture at  $40$ – $60^{\circ}$  with nitric and sulphuric acids; the *isopropyl* group is thus replaced by the nitro group.

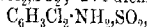
CHEMICAL ABSTRACTS.

**Condensation of Salicylaldehyde and Thymol. Synthesis of *o*-Hydroxyphenyldithymylmethane.** F. LAVILLA LLORENS (*Anal. Fis. Quim.*, 1920, **18**, 139–147).—The object of the investigation is to prepare triarylmethanes with a hydroxyl group on each benzene nucleus, and to study their physicochemical properties. The first of these compounds to be prepared is *o*-hydroxyphenyldithymylmethane,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\text{MePr}^i\text{OH})_2$ , colourless, oblique prisms containing  $1\text{EtOH}$ , m. p.  $185^{\circ}$ , from salicylaldehyde and thymol in presence of a small quantity of sulphuric acid. The *triacetyl* and *tribenzoyl* derivatives and the *trimethyl* and *triethyl* ethers are described; the last three compounds have m. p.  $126$ – $127^{\circ}$ ,  $137$ – $138^{\circ}$ , and  $77$ – $78^{\circ}$  respectively. A *tribromo* derivative,  $\text{C}_{27}\text{H}_{29}\text{O}_3\text{Br}_3$ , m. p.  $170^{\circ}$ , is obtained in acetic acid solution. The corresponding *tri-iodo* compound has m. p.  $111^{\circ}$ . The *trisodium* salt,  $\text{C}_{27}\text{H}_{29}\text{O}_3\text{Na}_3$ , crystals, is decomposed slightly by carbon dioxide. Amorphous precipitates are obtained: with lead salts, light yellow; copper salts, bluish-green; and ferric salts, yellowish-brown.

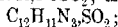
W. R. S.

**Molecular Compounds of Sulphur Dioxide with Amines.** A. KOREZYNSKI and M. GLEBOCKA (*Gazzetta*, 1920, **50**, i. 378–387).—The following compounds of sulphur dioxide with

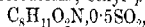
amines have been prepared: with *p*-toluidine,  $C_7H_7 \cdot NH_2 \cdot SO_2$ , canary-yellow;  $\alpha$ -naphthylamine,  $C_{10}H_7 \cdot NH_2 \cdot SO_2$ , orange-yellow; *p*-chloroaniline,  $C_6H_4Cl \cdot NH_2 \cdot SO_2$ , canary-yellow; *p*-bromoaniline,  $C_6H_4Br \cdot NH_2 \cdot 0.5SO_2$  and  $C_6H_4Br \cdot NH_2 \cdot SO_2$ , canary-yellow; 3:5-dichloroaniline,  $C_6H_3Cl_2 \cdot NH_2 \cdot SO_2$ ; 2:4-dichloroaniline,



canary-yellow; 3:5-dibromoaniline,  $C_6H_3Br_2 \cdot NH_2 \cdot SO_2$ , canary-yellow; *p*-nitrosodiethylaniline,  $C_8H_{10}O_2N_2 \cdot 2SO_2$ ; diphenylamine,  $C_{12}H_{11}N \cdot 0.5SO_2$ , orange;  $\alpha$ -naphthaquinoline, liquid compound;  $\gamma$ -chloroquinoline,  $C_{10}H_8NCl \cdot 1.5SO_2$ ; aminoazobenzene,

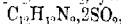


dimethylaminoazobenzene,  $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NMe_2 \cdot 0.5SO_2$ ; dimethylaminoazobenzoic acid,  $CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2 \cdot SO_2$ ; thiocarbamide,  $CH_3N_2S \cdot 0.5SO_2$ , colourless; ethyl *p*-aminobenzoate,



canary-yellow; *o*-aminocinnamic acid,  $C_9H_8O_2N \cdot SO_2$ , pale yellow;

2:4-tolylenediamine,  $C_7H_7N_2 \cdot SO_2$ , canary-yellow; *p*-nitro-*m*-phenylenediamine,  $C_6H_7O_2N_3 \cdot 0.5SO_2$ , yellow; benzidine,

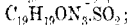


canary-yellow; 1:3-diaminoazobenzene,  $C_{12}H_{12}N_4 \cdot 0.5SO_2$ ; tetra-

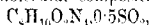
methylaminotriphenylmethane,  $C_{22}H_{26}N_6 \cdot 2.5SO_2$ ; leucaniline,

$C_{12}H_{21}N_3 \cdot 3SO_2$ , pale yellow; *p*-leucaniline,  $C_{19}H_{19}N_3 \cdot 1.5SO_2$ , pale

yellow; rosaniline,  $C_{20}H_{21}ON_3 \cdot 1.5SO_2$ ; pararosaniline,



dimethylaminoacetanilide,  $C_{11}H_{11}ON_2 \cdot SO_2$ , canary-yellow; hexamethylenetetramine absorbs 36.6--37.8%  $SO_2$ , giving a colourless product of no definite molecular composition; caffeine,



colourless; strychnine,  $C_{21}H_{22}O_4N_2 \cdot 2SO_2$ , pale yellow; brucine,

$C_{27}H_{30}O_4N_2 \cdot 3SO_2$ , yellow; morphine,  $C_{17}H_{19}O_4N \cdot 1.5SO_2$ , canary-

yellow; quinine,  $C_{20}H_{24}O_4N_2 \cdot SO_2$ , lemon-yellow; papaverine,

$C_{20}H_{23}O_4N \cdot SO_2$ , straw-yellow; veratrine,  $C_{32}H_{39}O_8N_2 \cdot 2.5SO_2$ , yellow;

hematin,  $C_{54}H_{56}O_4N_4Fe \cdot 2.5SO_2$ ; atropine, cocaine, and narcotine

form liquid additive compounds with sulphur dioxide, and no

additive compounds are given by *o*-, *m*-, and *p*-nitroanilines,

2:4- and 3:5-dinitroanilines, trinitroaniline, 6-halogeno-2:4-di-

nitroanilines, *p*-nitrosoaniline, trihalogenated anilines, *m*- and

*p*-nitrodimethylanilines, azobenzene, benzeneazobenzene, ethyl

ether, dimethylaminoazobenzene, carbamide, acetamide,

benzamide, asparagine, thiocarbamide, acetanilide, acetophenetide,

$\alpha$ -aminopropionic acid,  $\alpha$ -aminoisobutyric acid, aminobenzoic acids,

sulphanilic acid and its sodium salt, propyl *p*-aminobenzoate,

*m*- and *p*-aminocinnamic acid, *o*-, *m*-, and *p*-aminophenols, *p*-chloro-

*o*-aminophenol, ethyl *p*-amino-*m*-hydroxybenzoate, methyl *m*-amino-

*p*-hydroxybenzoate, carbazole, *p*-benzoquinone, distyryl ketone,

theobromine, and haemin.

When kept in a desiccator, the above additive compounds lose sulphur dioxide; measurements of the pressures developed in this way are now being made.

The following general conclusions are drawn from the results obtained. Sulphur dioxide unites equally with primary, secondary,

and tertiary amines. Colourless amines containing an aromatic nucleus yield yellow additive compounds, whilst those free from such nucleus give colourless compounds. The appearance of the colour indicates the formation of secondary compounds, which are produced by virtue of the secondary valencies of the nitrogen atom. The action of such secondary valencies is diminished or entirely removed by the presence of negative substituents in the molecule, the influence of a nitro- or hydroxyl group being greater than that of a halogen atom. No direct dependence exists between the number of amino-groups and the number of molecules united with  $\text{SO}_2$ . In compounds of complicated structure, such as the alkaloids, the number of molecules united with  $\text{SO}_2$  is mostly greater than the number of nitrogen atoms.

When thoroughly dried reagents are used, carbon dioxide and hydrogen sulphide do not form additive compounds with *p*-toluidine,  $\alpha$ -naphthylamine,  $\alpha$ -naphthaquinoline, brucine, hæmin, or hæmatin. Similar failure to form compounds, even with ferrous sulphate and ferrous ammonium sulphate, is exhibited by nitric oxide.

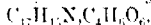
T. H. P.

**Syntheses of *s*-Xylidine.** HERBERT L. HALLER, ELLIOT Q. ADAMS, and EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1920, **42**, 1840—1842).—*s*-Xylidine may be prepared from mesitylene by passage through mesitylenic acid and its amide, the latter being converted into the amine by Hofmann's reaction. A more satisfactory process is a modification of that of Willgerodt and Schmierer (*A.*, 1905, i, 425), starting from *m*-4-xylidine. The authors find that, in this process, nitroacetylxylidide may be converted directly into nitroxylene by heating the xylidide for fifteen minutes with sulphuric acid (D 1.84), pouring the product into a mixture of ethyl alcohol and sulphuric acid, diazotising with sodium nitrite, and distilling the product with steam in the presence of copper powder. *s*-Xylidine has m. p. 139.6—140.2°,  $n_D^{20}$  1.45,  $n_D^{169}$  1.69.

W. G.

**Separation of  $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane into its Optical Antipodes.** S. BERLINGOZZI (*Gazzetta*, 1920, **50**, ii, 56—59).—This compound, obtained as the racemic modification (this vol., i, 480), may be separated into its enantiomorphous components by fractional crystallisation of the tartrate from alcoholic solution.

*d*- $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane hydrogen tartrate,



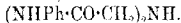
forms shining, white scales, m. p. 190—207° (decomp.). The free *d*-base,  $\text{C}_{17}\text{H}_{15}\text{N}$ , crystallises in white, translucent, triangular, or trapezoidal prisms, m. p. 81—82°,  $[\alpha]_D^{20} + 63.61^\circ$ . The *hydrochloride*,  $\text{C}_{17}\text{H}_{15}\text{N}, \text{HCl}$ , forms silky, white needles, m. p. 275—280° (decomp.),  $[\alpha]_D^{20} - 53.43^\circ$ .

*l*- $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane hydrogen tartrate forms tufts of white needles, m. p. 195—210° (decomp.). The free *l*-base crystallises in white, translucent, triangular prisms, m. p. 81—82°,  $[\alpha]_D^{20} - 63.38^\circ$ . The *hydrochloride* forms silky, white needles, m. p. 275—280°,  $[\alpha]_D^{20} + 53.18^\circ$ .

T. H. P.

**Amines. VIII. The Preparation of *o*-Aminoacetanilide.**

ARTHUR J. HILL and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1704—1711. Compare Dubsky and Granacher, A., 1918, i, 189).—To obtain a satisfactory yield of *o*-aminoacetanilide, the authors found it necessary to modify Majert's process (D.R.-P. 59121). The chloroacetanilide (550 grams) was added to 11 kilos. of 95% alcohol previously saturated with ammonia. The mixture was kept for five days at 20°, and then evaporated under diminished pressure to one-quarter of its volume. The liquid was poured into 3.5 litres of water, and the oil which separated was filtered after it had solidified. Aminoacetanilide was obtained from the filtrate by evaporating it nearly to dryness, and then recrystallising the residual material from water. The oil which separated and then solidified, as described above, was iminodiacetanilide,



In some preparations, a small amount of *nitrilotriacetanilide*,  $(\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2)_3\text{N}$ , m. p. 238—239°, was isolated.

The authors were unable to obtain satisfactory yields of aminoacetanilide by Majert's process (D.R.-P. 59874) from aniline and ethyl aminoacetate hydrochloride.

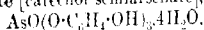
W. G.

**Preparation of "Cupferron."** D. B. KASANOF (*J. Ind. Eng. Chem.*, 1920, **12**, 799).—The yield of the intermediate substance, phenylhydroxylamine, in the preparation of "cupferron" (A., 1911, ii, 939) depends on the quality of the zinc dust used to reduce the nitrobenzene, but consistently good yields may be obtained if the zinc dust is previously treated with 2% mercurous nitrate solution slightly acidified with nitric acid.

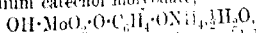
W. P. S.

**Crystallographic Properties of some Catechol Derivatives of Acids of Heavy Metals and their Salts.** P. J. BEGER (*Centr. Min.*, 1920, 129—142).—The compounds, the crystallographic properties of which are described in considerable detail, were prepared by Weinland and his collaborators (A., 1919, i, 442).

Triccatechol arsenate [catechol semiararsenate],



small, shining, colourless crystals of cubic habit, belonging to the rhombic, bipyramidal system,  $a:b:c=0.958:1:0.988$ . There are perfect cleavages parallel to the three pinacoid faces. Optic axial plane, {010}. The chromium salt,  $[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]_2\text{H}_2\text{Cr}\cdot 12\text{H}_2\text{O}$ , the cobalt salt,  $[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]_2\text{H}_2\text{Co}\cdot 8\text{H}_2\text{O}$ , and the corresponding nickel salt, all crystallise in the cubic system. The sodium salt of the nickel derivative,  $\text{Ni}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{ONa})_3\cdot 12\text{H}_2\text{O}$ , forms greenish-black, monoclinic, prismatic crystals, the axial ratios of which could not be completely determined;  $a:b:c=1.19:1:1$ ;  $\beta=102.5^\circ$  approx. Ammonium catechol molybdate,



forms reddish-black prisms, rhombic bipyramidal,  $a:b:c=0.5890:1:0.9105$ . The crystals, which sometimes show vicinal faces with complex indices, cleave perfectly parallel to {010} and {001}.

E. H. R.

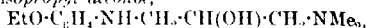


**Quinol.** J. MESSNER (*Pharm. Zentr.-h.*, 1920, 61, 454—455).—The statement found generally in literature that quinol reduces Fehling's solution in the cold and silver nitrate only when heated is incorrect. Quinol reduces silver nitrate at the ordinary temperature, with the separation of metallic silver; it at once changes the colour of Fehling's solution to green, but a precipitate of cuprous oxide forms only after long contact or when the mixture is heated. The reactions are therefore of little use for distinguishing quinol from catechol.

W. P. S.

**Amino-alcohols Derived from  $\alpha$ -Anilino- $\gamma$ -dialkylaminoisopropyl Alcohols.** E. FOURNEAU and J. RANERO (*Anal. Fis. Quim.*, 1920, 18, 133—139).—The physiological effect of the replacement of a phenoxy- by an anilino-group in amino-alcohols derived from aniline and its homologues was investigated. The aromatic amine was made to react with epichlorohydrin, and the derivative thus obtained treated with dimethylamine or one of its homologues.

The following substances are described:  $\alpha$ -p-phenetidin- $\gamma$ -dimethylaminoisopropyl alcohol,



b. p.  $212^\circ/14$  mm., m. p.  $79^\circ$ ;  $\alpha$ -p-toluidino- $\gamma$ -dimethylaminoisopropyl alcohol,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p.  $190^\circ/12$  mm., m. p.  $72^\circ$ ;  $\alpha$ -methylanilino- $\gamma$ -dimethylaminoisopropyl alcohol,  $\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p.  $168^\circ/14$  mm.;  $\alpha$ -anilino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $195^\circ/21$  mm., m. p.  $84^\circ$ ;  $\alpha$ -ethylanilino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $195^\circ/15$  mm.;  $\alpha$ -m-nitroanilino- $\gamma$ -dimethylaminoisopropyl alcohol, m. p.  $95^\circ$ ; and  $\alpha$ -o-anisidino- $\gamma$ -dimethylaminoisopropyl alcohol, b. p.  $198^\circ\text{--}200^\circ/30$  mm.

The anæsthetic action of benzoylmethylanilinodimethylaminoisopropyl alcohol hydrochloride is slower than that of stovaine; total anæsthesia is obtained in twenty minutes with  $N/50$ -solutions, and in seventeen minutes with  $N/25$ -solutions;  $N/25$  stovaine solutions, on the other hand, act in four to five minutes.

W. R. S.

**The Hydrobenzoin Transposition. Influence of the Nature of the Reagent.** M. TIFFENEAU and A. ORÉKHOFF (*Compt. rend.*, 1920, 171, 400—402. Compare Tiffeneau and Dorlenecourt, A., 1906, i, 724; Orékhoff, A., 1919, i, 272). With the exception of  $\alpha\beta$ -triphenylethanediol, which is really an aryl hydrobenzoin, the dehydration of the alkylhydrobenzoins may take place in several different ways, depending on the concentration of the sulphuric acid used and the nature of the alkyl group.

Thus, with dilute sulphuric acid,  $\alpha\beta$ -diphenylbutane- $\alpha\beta$ -diol yields  $\alpha\alpha$ -diphenylbutaldehyde, but with concentrated sulphuric acid it gives ethyldeoxybenzoin and diphenylmethyl ethyl ketone.  $\alpha\beta$ -Diphenylpropane- $\alpha\beta$  diol, on the other hand, only yields methyldeoxybenzoin with concentrated sulphuric acid.

W. G.

**The Hydrobenzoin Transposition. Influence of the *p*-Methoxyl Substitution on the Dehydration of Triarylethanediois.** A. ORSKHOFF and M. TIFFENBAU (*Compt. rend.*, 1920, 171, 473—476).—Under the influence of the same dehydrating agent, the triarylethanediois undergo change with or without molecular transposition. When the secondary alcohol group is attached to the same carbon atom as a phenyl group, there is no transposition, a ketone being formed. If the phenyl group is replaced by an anisyl group, there is transposition, with the formation sometimes of a single compound, a triarylacetaldehyde, the anisyl group migrating, sometimes with the formation of two compounds, the aldehyde and a ketone, in which case the phenyl group migrates. These reactions, simple and mixed, depend on the position of the hydroxyl group eliminated, and the stability of the hydroxyl groups appears to depend on the nature of the substituent groups. Thus *α*,*β*-dianisyl-*α*-phenylethanediois yields *pp'*-dimethoxytriphenylacetaldehyde,  $(C_6H_4OMe)_2CPh \cdot CHO$ , whilst *αα*-diphenyl-*β*-anisylethanediois yields *p*-methoxytriphenylacetaldehyde,  $OMe \cdot C_6H_4 \cdot CPh_2 \cdot CHO$ , and phenyl *p*-methoxydiphenylmethyl ketone,  $OMe \cdot C_6H_4 \cdot CHPh \cdot CPh_2$ .

W. G.

**Preparation of Mercury Compounds of Sulphophenolcarboxylic Acids and their Homologues which yield Colloidal Solutions with Water.** SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG LIST & Co. (D.R.-P. 321700; from *Chem. Zentr.*, 1920, iv, 292).—(i) The mercuration of the sulphophenolcarboxylic acids is effected in acid solution. (ii) The solutions of sulphophenolcarboxylic acids or their homologues are warmed or allowed to remain in contact with solutions of mercury salts, or the aqueous solutions of the sulphocarboxylic acids are similarly treated with an amount of mercuric oxide insufficient for the saturation of the three acidic groups (less than 1.5 molecules of oxide for each molecule of sulphophenolcarboxylic acid). Alternatively, the mercury compounds of the sulphophenolcarboxylic acids, which are sparingly soluble or insoluble in water, are warmed with acids or mixtures or compounds containing mercury and salicylic acid, or its homologues are treated at the ordinary or elevated temperature with concentrated sulphuric acid, and subsequently with a dilute acid. *Mercurisulphosalicylic acid* (from 5-sulphosalicylic acid) and *mercurisulpho-*m*-cresotic acid* form colourless crystals, very sparingly soluble in organic media, readily soluble in water to colloidal, viscous solutions.

H. W.

**Reduction of *o*-Benzoicsulphinide ["Saccharin"].** F. GIANFORMAGGIO (*Gazzetta*, 1920, 50, i, 327—340).—Previous investigations on reduction by means of amyl alcohol and sodium have been confined more especially to *o*-phenolcarboxylic acids, with which the benzene nucleus undergoes rupture between the hydroxyl and carboxyl groups, acids of the pimelic acid series being produced, and to *m*-phenolcarboxylic and *o*- and *p*-amino-

benzoic acids, which are reduced without rupture of the benzene ring.

In the reduction of *o*-benzoisulphinide by means of sodium and amyl alcohol, the nascent hydrogen formed eliminates the imino-group as ammonia, and also detaches the sulphonic group, which, after acidification, is liberated as sulphur dioxide; the final product of the reaction is hexahydrobenzoic acid, *o*-sulphobenzoic acid being probably formed as an intermediate product.

Of the various secondary products formed in reductions by means of sodium and amyl alcohol, owing to reactions between the alcohol and its sodium derivative (compare Einhorn and Lumsden, A., 1896, i, 45; Guerbet, A., 1899, i, 472), the author has identified only valeric acid.

A basic compound, which distils in a current of steam, is also formed in small proportion during the reduction of *o*-benzoisulphinide, and is to be investigated further. T. H. P.

**Action of Acetic Anhydride on  $\alpha$ -Naphthylpropionic Acid.** BYRON L. WEST (*J. Amer. Chem. Soc.*, 1920, **42**, 1656—1669).—When heated with potassium cyanide, sodium naphthalene- $\alpha$ -sulphonate gave  $\alpha$ -naphthonitrile, from which  $\alpha$ -naphthoamide was prepared. The latter, when reduced in alcoholic hydrochloric acid with sodium amalgam, gave  $\alpha$ -naphthylmethyl alcohol, which was readily oxidised to  $\alpha$ -naphthaldehyde. This aldehyde, when treated with malonic acid in the presence of alcoholic ammonia and subsequent addition of acid, gave a mixture of two acids, which, on heating, yielded  $\alpha$ -naphthylacrylic acid, m. p. 207·5°, giving an ethyl ester. On bromination, the ester gave ethyl  $\alpha\beta$ -dibromo- $\beta$ -1-naphthylpropionate,  $C_{10}H_7\cdot CHBr\cdot CHBr\cdot CO_2Et$ , which, with alcoholic potassium hydroxide, yielded  $\alpha$ -naphthylpropionic acid,  $C_{10}H_7\cdot C\equiv C\cdot CO_2H$ , m. p. 134—135°, giving a potassium salt.

When heated with acetic anhydride,  $\alpha$ -naphthylpropionic acid yielded 8- $\alpha$ -naphthylphenanthrene-6:7-dicarboxylic anhydride, m. p. 207—209° (compare Michael and Bucher, A., 1898, i, 256), from which a very insoluble sodium salt was prepared. The anhydride gave Baeyer's phthalein reaction and fluorescein test. W. G.

**Preparation and Properties of Cellulose Phthalate.** H. A. LEVEY (*J. Ind. Eng. Chem.*, 1920, **12**, 743—744).—Cellulose phthalate,  $C_{10}H_6O_4\cdot SC_6H_4O_2\cdot 1/2O\cdot 4H_2O$ , was prepared by heating cotton cellulose (previously converted into "hydrocellulose" by treatment with a solution of chlorine in glacial acetic acid) for twenty-four hours at 70° with phthalic anhydride and zinc chloride in the minimum quantity of ethyl phthalate (or acetic acid), washing the resulting ester, and drying it not above 70° in a vacuum. The cellulose phthalate thus obtained was insoluble in alcohol, ether, acetic acid, ethyl phthalate, and other ordinary solvents. The presence of zinc chloride or other condensing agent is essential for the esterification. Phthalic anhydride does not displace the acetate radicle from cellulose acetate or the nitrate radicle from cellulose nitrate, even when the zinc chloride is replaced by sulphuric acid. C. A. M.

**Catalytic Hydrogenation of Cholesterol and Cholesterylene.** F. F. NORD (*Biochem. Zeitsch.*, 1919, 99, 261—267).—

Cholesterol in acetone solution was reduced by hydrogen in the presence of colloidal palladium until no more of the gas was absorbed. The dihydrocholesterol,  $C_{27}H_{48}O$ , produced, m. p.  $141^{\circ}$ , formed an acetyl derivative, m. p.  $110^{\circ}$ . Cholesterylene was hydrogenised in the same way, and yielded cholestane, b. p.  $269\text{--}271^{\circ}/12\text{ mm.}$ ,  $[\alpha]_D^{25} + 43.32^{\circ}$ . S. S. Z.

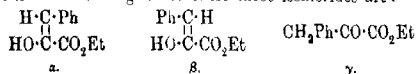
**Action of Alcoholic Sodium Acetate Solution on Cholesterol Dibromide.** A. WINDAUS and H. LÜDERS (*Zeitsch. physiol. Chem.*, 1920, 109, 183—185).—

The authors have prepared the so-called metacholesterol described by Lifschütz (A., 1919, i, 591), and find that: (1) it yields ordinary cholesterol dibromide, reduction of which gives cholesterol, m. p.  $146^{\circ}$ ; (2) its melting point is raised from  $141\text{--}142^{\circ}$  to  $145^{\circ}$  by repeated crystallisation from methyl alcohol; (3) the isobutyrate and acetate are identical with those prepared from cholesterol. The conclusion is drawn that "metacholesterol" consists principally of ordinary cholesterol.

T. H. P.

**Isomerism in the Series of Aromatic  $\alpha$ -Ketonic Acids.**H. GAULT and R. WEICK (*Compt. rend.*, 1920, 171, 395—398).—

It has previously been shown (this vol., i, 485) that ethyl phenylpyruvate can be obtained in two isomeric forms,  $\alpha$ -, m. p.  $51^{\circ}$ , and  $\beta$ -, b. p.  $149^{\circ}/15\text{ mm.}$  A third isomeride,  $\gamma$ -, m. p.  $79^{\circ}$ , has now been obtained by the action of sodium acetate on the  $\beta$ -isomeride. The constitutions assigned to these three isomerides are:



It is shown that the  $\alpha$ - and  $\beta$ -isomerides, when brominated in carbon disulphide solution at  $-15^{\circ}$ , give a dibromo-derivative,  $\text{CHPhBr}\cdot\text{CBr}(\text{OH})\cdot\text{CO}_2\text{Et}$ , m. p.  $55\text{--}60^{\circ}$ , which decomposes very rapidly at the ordinary temperature, losing hydrogen bromide and giving the compound,  $\text{CHPhBr}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , b. p.  $184^{\circ}/20\text{ mm.}$  The  $\gamma$ -isomeride is only brominated in boiling carbon disulphide, and gives ethyl  $\beta$ -bromo- $\alpha$ -keto- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone- $\gamma$ -carboxylate,  $\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\text{Ph}$ , m. p.  $151^{\circ}$ .

The  $\alpha$ - and  $\gamma$ -esters are converted into the  $\beta$ -ester by slow distillation under reduced pressure. The  $\beta$ - and  $\gamma$ -esters are converted into the  $\alpha$ -ester by shaking in ethereal solution with sodium carbonate, whilst the  $\beta$ -ester is converted into the  $\gamma$ -ester, as described above. W. G.

**Preparation of Aldehydes and Ketones.** CARL HARRIES (D.R.P. 321567; from *Chem. Zentr.*, 1920, iv, 292).—Ozonides are treated with reducing agents, particularly with potassium ferrocyanide, in the presence or absence of acids, whereby the formation of resins is considerably restricted. The solution of isoeugenol ozonide in ethyl acetate gives vanillin in 95% yield.

*n*-Oleic acid ozonide gives nonaldehyde. The ozonides from tar oil, gas oil, and the unsaturated oils, obtained by chlorination of crude paraffin and elimination of hydrogen chloride, yield mainly aldehydes in addition to ketones and small amounts of acids.

H. W.

**Manufacture of Protocatechualdehyde.** CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat. 145871).—The acid chloride of any suitable acyl derivative of protocatechuic acid, such as the diacetate, dibenzoate, carbonate, or di-*p*-toluenesulphonate, or of the dibenzyl ether of protocatechuic acid, is reduced to the corresponding derivative of protocatechualdehyde by treatment in an inert solvent at boiling temperature with hydrogen in presence of a hydrogenating catalyst, such as palladium or nickel. When the evolution of hydrogen chloride ceases, the reduction product is hydrolysed and protocatechualdehyde isolated as its bisulphite compound in the usual way.

G. F. M.

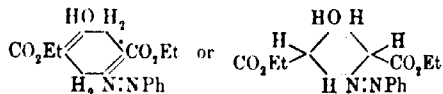
**Perfumes from Perillaldehyde.** S. FURUKAWA (Jap. Pat. 35332).—An alcoholic solution of the aldehyde (150 grams in 500 c.c.) is heated for two hours on the water-bath with hydroxylamine hydrochloride (70 grams) and sodium hydrogen carbonate (100 grams). The resulting oxime, *m. p.* 102°, is two thousand times as sweet as sucrose; it is easily converted into perillonitrile, *b. p.* 116–118° 11 mm., *D*<sub>4</sub><sup>15</sup> 0.94–0.949, which is two hundred times as sweet as sucrose, and is suitable as an ingredient of tooth-powders or perfumes.

CHEMICAL ABSTRACTS.

**The Isomerism of the Oximes. IX. 2:4-Dinitrobenzaloxime and Bromo-substituted Hydroxy- and Methoxybenzaloximes.** VERA WENTWORTH and OSCAR LISLE BRADY (T., 1920, 117, 1040–1045).

**Unsaturated Compounds in Organic Chemistry. II. Constitution of Succinylsuccinic Ester.** M. GIUA (*Gazzetta*, 1920, 50, i, 387–393). The action of phenylhydrazine and of *as*-phenylmethylhydrazine on ethyl succinylsuccinate has been investigated (compare Knorr and Bülow, A., 1884, 1380; von Baeyer, Jay, and Jackson, A., 1891, 1486; von Baeyer and von Brüning, A., 1891, 1486; Kijner, A., 1894, i, 67).

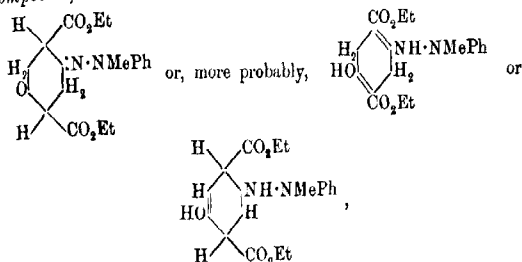
The action of phenylhydrazine (1 mol.) on ethyl succinylsuccinate (1 mol.) in alcoholic solution and in presence of acetic acid yields (1), as principal product, the compound,



which crystallises in carmine-red, prismatic needles, *m. p.* 142°, dissolves in sulphuric acid to a colourless solution, and is only slowly attacked by boiling concentrated alkali solution. Reduction of this compound by means of sodium and alcohol yields a violet

compound, which does not melt at  $240^{\circ}$  and dissolves in alkali solution with yellow coloration. (2) Ethyl benzenedihydrazodihydroterephthalate, m. p.  $204-205^{\circ}$  (compare Knorr, *loc. cit.*; von Baeyer, *loc. cit.*). The latter and its isomeride, m. p.  $166^{\circ}$ , form the principal products of the reaction when 2 mols. of phenylhydrazine are taken per 1 mol. of the succinylsuccinic ester. Whatever the proportions between the reacting compounds, the reaction yields always a viscous, tar-like resin, which partly decomposes, with formation of aniline, when distilled under a pressure of 52 mm.

The action of *as*-phenylmethylhydrazine on ethyl succinylsuccinate in alcoholic solution containing acetic acid yields the compound,



which crystallises in golden-yellow needles, m. p.  $135-136^{\circ}$ , and dissolves in concentrated sulphuric acid, giving a reddish-yellow solution. T. H. P.

**Manufacture of Aromatic Alkylamino-compounds [Alkylaminoanthraquinones].** FREDERICK WILLIAM ATTACK and WALTER NORMAN HAWORTH (Brit. Pat. 147964).—The aminoanthraquinones are alkylated by treatment with an alkyl sulphate in solution in a neutral medium of high boiling point, such as nitrobenzene or tetrachloroethane, in presence of a mild alkali, such as sodium carbonate. Thus 20 parts of 1-aminoanthraquinone may be dissolved in 216 parts of nitrobenzene and 20 parts of sodium carbonate added, the mixture being heated to boiling under a reflux condenser, while  $17\frac{1}{2}$  parts of methyl sulphate are added during the space of two hours. A yield of 87% of 1-methylaminoanthraquinone is obtained. When 5 parts of 2-aminoanthraquinone are similarly treated with 6 parts of methyl sulphate, 2-dimethylaminoanthraquinone is the chief product. G. F. M.

**Rhinanthocyanin.** A. NESTLER (*Ber. deut. bot. Ges.*, 1920, 38, 117—121).—When rhinanthin is extracted from the seeds of *Alectorolophus hirsutus* by means of 70% alcohol containing 5% of hydrochloric acid, the glucoside is gradually hydrolysed by the acid into a blue colouring matter, rhinanthocyanin, and a sugar. This hydrolysis may be effected also, although less rapidly, by sulphuric

oxalic, citric, lactic, or acetic acid, and the production of the so-called blue (mostly dark brownish-violet) bread is due to contamination of the flour with the meal of seeds containing rhinanthin and hydrolysis of the latter by means of the lactic acid formed during the fermentation. In the course of a few hours or days, the blue rhinanthocyanin solution becomes colourless and deposits blue or green granules, which sometimes retain their colour for many weeks, and sometimes turn brown. Rhinanthocyanin imparts a blue or green coloration to chloroform, but does not dissolve therein; the colour is due to the presence of granules,  $0.7-1\mu$  in size, and of droplets of  $2.5-7\mu$ , and is removable by ultra-filtration.

T. H. P.

### Chitin and Chitin Derivatives of Animal and Plant Origin.

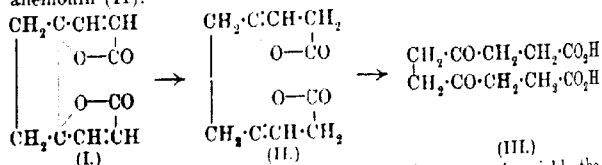
O. SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1920, **87**, 74-86).

—Chitin was prepared by dissolving moulds, previously freed from cellulose, in concentrated hydrochloric acid and filtering; the chitin was then precipitated from the filtrate by the addition of water and washed until free from chloride. From the elementary analysis, the formula  $C_{34}H_{56}O_{22}N_4$  was calculated, which suggests that the chitin lost one acetyl group in the treatment with hydrochloric acid. It seems to resemble chitin of animal origin, with the exception that it is less resistant to the action of acids and alkalis. A compound resembling Winterstein's paralextran was prepared by the author from mould cellulose. The work of previous investigators on chitin is reviewed.

S. S. Z.

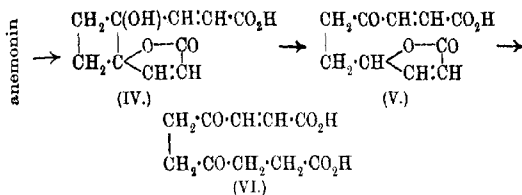
### Transformations of Anemonin by Acids and Alkalis. VI.

Y. ASAHINA and A. FUJITA (*J. Pharm. Soc. Japan*, 1920, No. 461. Compare A., 1892, i, 241; 1896, i, 623; 1899, i, 930; 1914, i, 561; 1915, i, 1067; 1916, i, 401; this vol., i, 70, 321, 493).—Having settled the constitution of anemonin (I) by synthesis (this vol., i, 493), the authors now explain its transformations. Cold sulphuric acid is without action; the hot, dilute acid changes it to anemoninic acid (VI). Cold concentrated hydriodic acid dissolves the substance, and, on keeping, anemonolic acid (III) separates quantitatively, probably after intermediate formation of dihydro-anemonin (II).

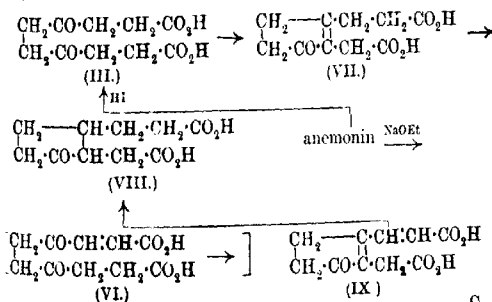


When warmed with methyl-sulphuric acid, anemonin yields the methyl ester,  $C_{12}H_{14}O_5$ , m. p.  $62^\circ$ , of furan-2-propionic-5-acrylic acid, m. p.  $179^\circ$ . This acid is reduced by sodium amalgam to furan-2:5-dipropionic acid, which is also formed by prolonged heating of anemonolic acid above its melting point. The authors cannot confirm the higher melting point of furan-2-propionic-5-acrylic acid given by Cooper and Nuttall (T., 1914, **105**, 2218).

Concentrated potassium carbonate solution changes anemonin into anemoninic acid (VI), which can be isolated in a 10% yield as crystals of the  $\alpha$ -variety, m. p. 117°. This is readily transformed by concentrated hydrochloric acid at 60° to the  $\beta$ -variety, m. p. 189°. The two forms are probably *cis-trans*-modifications. Both yield with ammonia an impure pyrrole derivative. The  $\beta$ -acid yields with concentrated sulphuric acid and methyl alcohol its own methyl ester, m. p. 128°, together with that of furan-2-propionic-5-acrylic acid (above). Anemoninic acid is oxidised by permanganate to acetonediacetic ( $\gamma$ -ketopimelic) acid. The formation of anemoninic acid (VI) from anemonin is represented as follows; IV and V are hypothetical:



Sodium and 98% alcohol transform anemonin into  $\alpha$ -anemononic acid (IX), m. p. 120°, which is changed by heating with concentrated hydrochloric acid to the stereoisomeric  $\beta$ -variety, m. p. 210°. Both are reduced catalytically to the same tetrahydroanemononic acid (VIII), m. p. 135°. Anemononic acid (III) is transformed by alcoholic potassium hydroxide at the ordinary temperature to *unhydroanemononic acid* (VII),  $\text{C}_{10}\text{H}_{12}\text{O}_5$ , m. p. 129°, yielding a *semicarbazone*, m. p. 208°. This acid combines with one molecule of hydrogen catalytically, and is then found to be identical with tetrahydroanemononic acid (VIII), formed by reduction of anemononic acid, whence the constitution IX is deduced for the latter. Its formation from anemonin by sodium ethoxide is attributed to the intermediate formation of anemoninic acid (VI), although the latter itself could not be converted into anemononic acid.



G. B.



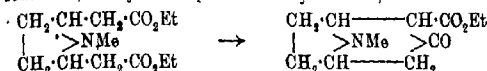
**Nature of the Red Dye of Crustaceæ.** J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 963—964; from *Chem. Zentr.*, 1920, iii, 259).—The red dye of crustaceæ behaves in the same manner as carotin towards solvents. The latter also yields a violet-brown additive compound with iodine and a blue coloration with sulphuric acid. The absorption bands of both dyes are similar. The dye of the crustaceæ is a compound with carbon and hydrogen in the ratio 5:7, and, according to ebullioscopic determinations, has the empirical formula  $C_{40}H_{56}$ .  
H. W.

**A Comparative Study in the Xanthone Series. I.** SURENDRA NATH DHAR (*T.*, 1920, **117**, 1053—1070).

**Preparation of Derivatives of Hydrastinine.** KARL W. ROSENEMUND (D.R.-P. 320480; from *Chem. Zentr.*, 1920, iv, 223).—The process depends on (i) the treatment of methylenedioxyphenylisopropylamine with formaldehyde or substances which yield formaldehyde and catalytically active agents, and oxidation of the condensation product thus formed; (ii) the condensation of methylenedioxyphenylisopropylamine with formaldehyde or substances which yield formaldehyde, transformation of the alkylideneamine thus produced with the aid of active catalysts, alkylation, and oxidation of the substance so formed; (iii) the use of iodine as oxidising agent. 6:7-Methylenedioxy-3-methyltetrahydroisoquinoline, m. p. 65–67°, is obtained by heating the oily product of the action of calculated quantities of methylenedioxyphenylisopropylamine and formaldehyde with hydrochloric acid (25%) at 100°. The base is converted by methyl iodide into 3-methyldihydrohydrastinine hydriodide, m. p. 240°; the free base has m. p. 86°, whilst the hydrochloride has m. p. 230°. The hydrochloride is directly obtained when methylenedioxyphenylisopropylamine hydrochloride (1 part) and commercial formaldehyde solution (2 parts) are heated for three hours at 130–135°. 3-Methyldihydrohydrastinine is converted by iodine and potassium acetate in alcoholic solution into 3-methyldihydrohydrastinine hydriodide, m. p. 207° (base, m. p. 103–104°). The dichromate, obtained by the action of potassium dichromate and sulphuric acid on an aqueous solution of 3-methyldihydrohydrastinine hydrochloride, is oily. 3-Methyl-N-ethylhydronorhydrastinine hydriodide separates on boiling a solution of 3-methyldihydronorhydrastinine in benzene, and is oxidised to 3-methyl-N-ethylnorhydrastinine (hydriodide, yellow crystals, m. p. 210°). The products are less toxic than hydrastinine.  
H. W.

**Preparation of Tropinonecarboxylic Esters.** R. WILLSTÄTTER (D.R.P. 302401; from *Chem. Zentr.*, 1920, iv, 42–43).—N-Methylpyrrolidinediacetic esters are treated with an alkali metal or other condensing agent. The initial material for the synthesis is succinylidiacetic ester, which is transformed by methylamine in

acetic acid solution, for example, into the corresponding *N*-methylpyrrolidinediacetic ester; the latter is reduced by hydrogen in the presence of platinum in acetic acid solution to *N*-methylpyrrolidinediacetic ester. The diethyl ester is a colourless, mobile oil with an alkaline reaction, b. p. 162.5°/9 mm., whilst the methyl ester has b. p. 155.5°/12 mm. The *N*-methylpyrrolidinediacetic esters lose alcohol under the influence of sodium, sodium alkoxides, or sodamide, and yield tropinonecarboxylic esters,

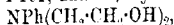


For further preparations, the ester is only obtained in solution or mixed with sodium salts; its separation from admixture with organic substances is difficult, since it is very readily decomposed and resinified; it is very slightly soluble in water and exhibits a strong ferric chloride reaction. Ethyl tropinonecarboxylate is converted by warm dilute acid into tropinone, which can be isolated in substance or as the picrate or dibenzylidene derivative; it is reduced electrolytically or by sodium amalgam to *r*-ecgonine ester.

H. W.

**Heterocyclic Compounds of *N*-Arylamino-alcohols.** R. E. RINDFUSZ and V. L. HARNACK (*J. Amer. Chem. Soc.*, 1920, **42**, 1720—1725).—Aniline condenses with trimethylene chlorohydrin to give *γ*-hydroxypropylaniline,  $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , b. p. 192°/30 mm.,  $n_D^{20}$  1.502,  $D_4^{20}$  1.063, and *di-γ*-hydroxypropylaniline,  $\text{NPh}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH})_2$ , b. p. 241—242°/25 mm.,  $n_D^{24}$  1.565,  $D_4^{26}$  1.097. When dehydrated by phosphoric oxide, the first-named compound yields tetrahydroquinoline, whilst the second yields julolidine. Tetrahydroquinoline, when condensed with allyl bromide, gives 1-allyltetrahydroquinoline, b. p. 135°/25 mm.,  $n_D^{24}$  1.556,  $D_4^{24}$  1.024, and with trimethylene chlorohydrin gives 1-*γ*-hydroxypropyltetrahydroquinoline, b. p. 227—229°/18 mm.,  $n_D^{21}$  1.561,  $D_4^{27}$  1.091, which, on dehydration, yields julolidine.

*β*-Hydroxyethylaniline,  $\text{NHPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , has b. p. 188°/30 mm.,  $n_D^{24}$  1.576,  $D_4^{24}$  1.101, and *di-β*-hydroxyethylaniline,



has b. p. 228°/15 mm., m. p. 53.5—54°. *β*-Hydroxyethylaniline on dehydration gives diphenylpiperazine, and *di-β*-hydroxyethylaniline yields phenylmorpholin.

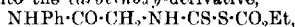
W. G.

**The Cyanine Dyes. II. The Synthesis of *o*-Amino-cinnamylidenequinaldine Methiodide.** WILLIAM HOBSON MILLS and PERCY EDWIN EVANS (*T.*, 1920, 117, 1035—1040).

**Thiocyanates and Thiocarbimides. XIV. A New Method of Synthesising 2-Thiohydantoins.** TRENT B. JOHNSON, ARTHUR J. HILL, and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1920, **42**, 1711—1720).—*o*-Aminoacetanilide reacted with carbon disulphide

in alcoholic solution to give the unstable *ω*-aminoacetanilide salt of the corresponding dithiocarbamic acid,

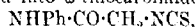
$\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{SH}\cdot\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ ,  
m. p. 145° (decomp.), which, by the action of ethyl chloroformate, was converted into the carbethoxy-derivative,



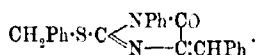
and this, on distillation, yielded 2-thio-1-phenylhydantoin. This thiohydantoin, when digested with chloroacetic acid, was converted into 1-phenylhydantoin.

When ethyl chloroformate acted directly on *ω*-aminoacetanilide, *ω*-carbethoxyaminoacetanilide, m. p. 137.5°, was obtained, which was converted by the action of alcoholic potassium hydroxide into 1-phenylhydantoin.

The dithiocarbamate (above), when digested with mercuric chloride, was converted into *ω*-thiocarbinidoacetanilide,

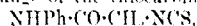


which spontaneously and immediately condensed to give 2-thio-1-phenylhydantoin, the benzylidene derivative of which condensed with benzyl chloride in the presence of sodium ethoxide to give 2-benzylthiol-1-phenyl-4-benzylidenehydantoin,



m. p. 178°.

The spontaneous change of the thiocarbimide,



into 2-thio-1-phenylhydantoin, and the series of changes described above, are taken as strong support of the view that the conversion of compounds of the type  $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Cl}$  into  $\psi$ -thiohydantoins, is by passage through the normal thiocyanate (A. 1918, i, 256), and not through the thiocarbimide (Beckurts and Frerichs, A., 1915, i, 792, 799). W. G.

### Preparation of Isatin and its Substitution Products

J. R. GEIGY (D.R.P. 320547; from *Chem. Zentr.*, 1920, iv, 223).—*ω*-Oximinoacetanilide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CH}(\text{N}\cdot\text{OH})$ , or its halogen alkyl, alkyloxy-, or carboxyl substitution products, which are capable of condensation, are warmed with concentrated sulphuric acid, and the isatinimines, of the general formula  $\text{R}\begin{array}{l} \nwarrow \text{NR} \\ \nearrow \text{C}(\text{NH}) \end{array}\text{CO}$  (in which R represents a substituted or unsubstituted benzene nucleus and R' a hydrogen, alkyl, or arylalkyl group), which are thus formed are decomposed by water into isatins and ammonia. The following examples are cited: isatin from *ω*-oximinoacetanilide; 5-methylisatin from *ω*-oximinoaceto-*p*-toluidide; 4-chloro-1-methoxyisatin, m. p. 240°, from chloro-*ω*-oximinoacetanilide; isatin-*o*-carboxylic acid, m. p. 235°, from *ω*-oximinoacetylanthranilic acid; 5-chloroisatin from *p*-chloro-*ω*-oximinoacetanilide; 4:7-dichloroisatin, orange-yellow crystals, from 2:5-dichloro-*ω*-oximinoacetanilide; *N*-ethyl- $\psi$ -isatin, dark red crystals, from *ω*-oximinoaceto-

ethylanilide; *N*-benzyl- $\psi$ -isatin, orange-yellow substance, from  $\alpha$ -oximinoacetobenzylanilide. H. W.

**Changes in the Physical State of Colloids. XXIII. Acid-albumin.** MONA ADOLF and ERNST SPIEGEL (*Biochem. Zeitsch.*, 1920, **104**, 175—189).—In the conversion of serum-albumin into acid-albumin by the action of boiling hydrochloric acid, the protein molecule changes in its acid-combining, but not in its alkali-combining, power. One gram of acid-albumin combines at most with 25 millimols. of sodium hydroxide, the equivalent weight of the acid-albumin being thus 416, which is the value found for the natural serum-albumin. The acid-combining power of acid-albumin is, however, 20% higher than that of the albumin itself. The values for the viscosity of acid-albumin solution are higher than those of the protein, but they exhibit the same changes on addition of acid or alkali, these changes being hence due to similar ionisation influences.

On addition of alkali hydroxide or acid to a solution of the natural albumin, the rotatory power reaches a maximum corresponding with the maximum of acid or alkali-combining power, this maximum persisting even when the excess acidity for a 1% solution amounts to 0.1*N*. When hydrochloric acid is added to an acid-albumin solution, the rotatory power changes and shows a distinct maximum at 0.058*N*-acidity, but diminishes at higher acidities; the maximum rotation corresponds, not with the maximum of ionisation indicated by the viscosity curve, but with an appreciably higher acidity. According to conductivity measurements, acid-albumin in neutral salts is tervalent, the velocity of migration being  $V=41.1$ .

Addition of salts of the heavy metals precipitates acid-albumin when dissolved in sodium hydroxide solution, but not when dissolved in hydrochloric acid; this precipitation hence represents a reaction only for the negative protein ion. T. H. P.

**Changes in the Physical State of Colloids. XXIV. Precipitation of Protein by Acids and Alkalies.** RICHARD WAGNER (*Biochem. Zeitsch.*, 1920, **104**, 190—199. Compare Pauli and Handovsky, A., 1909, i. 618; Pauli and Wagner, A., 1910, ii. 830).—Results are given of investigations on (1) the concentrations of a number of different acids just sufficient to produce flocculation in serum-albumin, (2) the viscosities of serum-albumin containing various acids in the concentration 0.05*N*, and (3) the swelling of gluten in 0.05*N*-acid. From these results, the conclusions are drawn that the state of the protein salt, as regards hydration and ionisation, conditions the precipitability of this salt in excess of acid, and that there is no reason to suppose that this precipitability is not primarily to be considered as displacement of a salt from solution by excess of its acid.

According to the author's views on the mode of salt-formation between alkali and protein, relations similar to the above should

hold in this case, and this is actually found with pure serum-albumin and alkali hydroxide in concentrations exceeding 5*N*.

T. H. P.

**Some Properties of Serin.** M. PIETTRE and A. VILA (*Compt. rend.*, 1920, 171, 371—373).—Serin, as prepared from the serum of horse blood by the method previously described (*ibid.*, 170), is soluble in water even after drying at 40° or in a vacuum over sulphuric acid. It has  $[\alpha]_D -57^\circ$  to  $-58^\circ$ , and contains much higher percentages of sulphur and calcium than the corresponding serum globulin. It exhibits the property of separating from its solution in an almost solid, granular mass at 0°, and dissolving again at the ordinary temperature.

W. G.

**Changes in the Physical Condition of Colloids. XXII. The General Chemistry of the Caseinates. II.** WOLFGANG PAULI and JOHANN MATULA (*Biochem. Zeitsch.*, 1919, 99, 219—236. Compare Pauli, A., 1915, i, 1016).—Conductivity experiments show that there are two zones in the reaction of casein with alkali hydroxide. In one zone, in which the reaction is neutral, the valency of the caseinate ions remains constant, whilst the conductivity increases slightly. In the second zone, when more alkali is added, both the valency and the conductivity of the caseinate ions increase. It is deduced from the conductivity curves that there exists a neutral tribasic caseinate which can take up more caseinogen without changing its valency.

S. S. Z.

**Causes of the Conductivity of Casein Solutions.** L. MÁNDOKI and M. POLÁNYI (*Biochem. Zeitsch.*, 1920, 104, 254—258).—Measurements of the electrical conductivity of neutral casein solutions show that the protein in solution is not a good conductor, so that the conductivity of these solutions must be due largely to decomposition products of the casein (compare Laqueur and Sackur, A., 1903, i, 300; Robertson, "Physical Chemistry of the Proteins").

T. H. P.

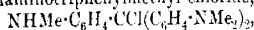
**Benzene Derivatives in Glutin and Protein-content of Gelatin.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, 109, 32—48. Compare A., 1919, i, 502). The author has investigated the benzene derivatives formed when the best commercial gelatin is subjected in solution at 40° to the action of a maceration of putrefying meat in presence of potassium dihydrogen phosphate, magnesium sulphate, sodium carbonate, and, in some cases, sodium potassium tartrate. The products identified comprise: (1) Traces of an indole derivative. (2) About 0.11% of aromatic hydroxy-acids, calculated on the anhydrous, ash-free material, indicating that gelatin contains the tyrosine group in appreciable proportion; succinic acid, derived from the aspartic acid of the gelatin, is also

found in small quantity. (3) At least 1.3% of phenylpropionic acid. It has also been found possible to isolate a protein from gelatin.

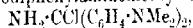
T. H. P.

**Prosthetic Group of Blood Pigment. Action of Diazomethane on certain Colouring Matters and on Anhydrous Ferric Chloride.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1920, 109, 108—116).—According to the ordinary formula for hæmin, the chlorine is assumed to be united to iron, although union with nitrogen is not excluded. In the action of diazomethane on different hæmins showing marked differences as regards esterification, removal of the halogen has never been observed. The author [with O. KUSCH] has now investigated the action of diazomethane on the hydrochlorides of various colouring matters of known constitution, and also on anhydrous ferric chloride. The results obtained indicate that true hæmins are allied rather to this anhydrous chloride, which is altered but little by diazomethane, than to the hydrochlorides of di- and tri-phenylmethane dyes, from which hydrogen chloride is very easily withdrawn, with formation of methyl chloride. With the hydrochloride of a furyl-methylindolenylmethane, the reaction is less ready, and with crystal-violet reduction to the leuco-base takes place. Finally, with a rhodamine hydrochloride no esterification occurs, so that the carboxyl group cannot be free, and an oxonium grouping must be assumed (compare Noeltling and Dziewoński A., 1905, i, 935).

The action of diazomethane on *P. ageratum coeruleum*, that is, on pentamethyltri-aminotriphenylmethyl chloride,

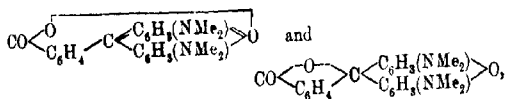


results in removal of 86.7% of the halogen. With *P. aureum*, that is, tetramethyldiaminodiphenylaminomethyl chloride,



79.2% of the chlorine is withdrawn.

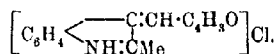
Tetramethylrhodamine hydrochloride,  $\text{C}_{21}\text{H}_{28}\text{O}_3\text{N}_2\text{Cl}$ , obtained from dimethyl-*m*-aminophenol and phthalic anhydride, forms green plates with metallic lustre, m. p. (dry) 288–290°, and dissolves in water or alcohol, giving a carmine-red solution showing orange-yellow fluorescence. The free base is obtained in green leaflets exhibiting metallic lustre, and dissolves sparingly in ether or light petroleum, and more readily in benzene, toluene, or xylene, giving colourless solutions. The constitutions of the coloured and colourless modifications of the base are



respectively. In benzene solution, the anhydrous base is unaltered by diazomethane, which, however, withdraws 97.4% of the chlorine from the hydrochloride, but does not esterify the base. The methyl ester of tetramethylrhodamine,  $\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2$ , obtained by passing

hydrogen chloride into a solution of the hydrochloride in methyl alcohol, forms violet-red needles, m. p. 190°, is insoluble in 5% sodium carbonate solution at the ordinary temperature, but dissolves, with hydrolysis, in cold 1% sodium hydroxide solution, giving a red solution; it is soluble also in hydrochloric acid with a red coloration.

*Furyl- $\alpha$ -methylindolenglymethane hydrochloride,*



prepared from furfuraldehyde and 2-methylindole, forms spherical aggregates, m. p. 300° (decomp.), the base being obtained as a brown precipitate on addition of sodium hydroxide solution. When suspended in acetone and treated with diazomethane, the hydrochloride loses nearly all its chlorine.

From an ethereal solution of ferric chloride, diazomethane withdraws 6.71% of the chlorine.

T. H. P.

**Calorimetric Investigations on Melanins.** FRANZ VON HOEFFET (*Biochem. Zeitsch.*, 1920, **104**, 1-8).—With the object of obtaining information indicative of the mechanism of formation of melanins, the author has determined the heats of combustion of various melanin preparations and of certain allied acids. The view that the formation of melanins in the integuments has its origin in tyrosine, or in the dihydroxyphenylalanine resulting from the oxidation of tyrosine, is not controverted by the author's results, the heat of combustion of tyrosine being of the same order of magnitude as that of the hippomelanin and that of one of the two liver melanins examined. On the other hand, the melanoidic acids formed during the hydrolysis of proteins by concentrated mineral acids are almost undoubtedly derived from tryptophan.

T. H. P.

**Hippomelanin. III.** OTTO RIESSER and PETER RONA (*Zeitsch. physiol. Chem.*, 1920, **109**, 16-31). The authors have repeated and extended their earlier work (*A.*, 1908, i, 1028; 1909, i, 749) on the decomposition of hippomelanin by the action of 3% hydrogen peroxide solution. The results obtained show that the criticisms of Adler-Herzmark (*A.*, 1913, i, 500) are not justified, and that the experiments made by this author were inadequate.

Great difficulty is experienced in ridding the melanin of admixtures, but, after thorough purification, the preparations obtained always gave guanidine and ether-soluble acids in small yields when subjected to oxidising decomposition by means of hydrogen peroxide. That the proportion of guanidine separated represents only a minimal value is shown by the observation that guanidine carbonate is largely destroyed by hydrogen peroxide at steam-bath temperature. When the action of the hydrogen peroxide is sufficiently protracted, a large proportion of the carbon of the melanin undergoes oxidation to carbon dioxide. Gradual

oxidation of melanin by means of hydrogen peroxide in ammoniacal solution promises to yield more characteristic decomposition products.

T. H. P.

**Relation of the Free Amino-groups to the Lysine Content in Proteins.** K. FÄLIX (*Zeitsch. physiol. Chem.*, 1920, 110, 217—229).—The author has estimated the nitrogen titratable with formalin in hydrolysed and unhydrolysed arachin (from *Arachis hypogaea*), glycimin (from *Soja hispida*), and gelatin, and draws the conclusion that the fraction of the hydrolysed protein which is precipitated by phosphotungstic acid after the removal of the other diamino-acids contains another nitrogenous substance besides lysine. The author further considers that Van Slyke's assertion (*A.*, 1914, i, 212) that the free amino-groups of unhydrolysed proteins contain exactly one-half of the nitrogen of the lysine in the protein molecule is not justified. He suggests that the grouping of the amino-acids in the molecule may vary with the individual protein.

S. S. Z.

**Chemical Constitution of Adenine Nucleotide and of Yeast-nucleic Acid.** W. JONES (*Amer. J. Physiol.*, 1920, 52, 193—202).—

When adenine nucleotide is hydrolysed by 5% sulphuric acid at 100°, the purine group is split off much more rapidly than the phosphoric acid; further, adenine nucleotide is a dibasic acid, indicating that only one hydrogen of the phosphoric acid has been replaced. These facts necessitate the union of phosphoric acid to carbohydrate, and that, in turn, to adenine. The structure of adenine nucleotide is thus similar to that of guanine nucleotide (*A.*, 1917, i, 597). When yeast-nucleic acid is hydrolysed with mineral acid, the rate at which phosphoric acid is set free corresponds practically with the composite rate calculated for a mixture of the four nucleotides. If yeast-nucleic acid is a chemical combination of the four nucleotides, then in this union the phosphoric acid group of the nucleotides is not disturbed and the nucleotide linkings cannot be through phosphoric acid groups. Adenine and guanine are split off from their respective nucleotides and from yeast-nucleic acid by acid hydrolysis with equal rapidity. This shows that in yeast-nucleic acid the linkings cannot be through the purine groups, and probably not through the pyrimidine groups. By this process of elimination, the nucleotide linkings in yeast-nucleic acid must be through the only remaining group, namely, the carbohydrate.

CHEMICAL ABSTRACTS.

**Action of Boiled Pancreas Extract on Yeast-nucleic Acid.**

W. JONES (*Amer. J. Physiol.*, 1920, 52, 203—207).—When an aqueous extract of pig pancreas is boiled and filtered, all its active agents but the one that decomposes yeast-nucleic acid into nucleotides, are destroyed. The extract will not act on thymus-nucleic acid. When yeast-nucleic acid is converted into nucleotides by this active agent, there is not the slightest change in acidity. This is regarded as the crucial test which proves that the nucleotide



linkings in yeast-nucleic acid are not through phosphoric acid groups. A structural formula for yeast-nucleic acid is suggested having the nucleotide linkings through the carbohydrate groups (compare preceding abstract).

CHEMICAL ABSTRACTS.

**Preparation of Adenine Nucleotide by Hydrolysis of Yeast-nucleic Acid with Ammonia.** W. JONES and A. F. ART (*Amer. J. Physiol.*, 1920, **50**, 574-578).—Adenine-uracil-dinucleotide as prepared by Jones and Germann (*A.*, 1916, i, 515) appears to be a mixture of adenine nucleotide and uracil nucleotide. Using the method of Jones and Kennedy (*A.*, 1919, i, 360), the authors separated from the mixture adenine nucleotide, which had the composition required by the formula  $C_{10}H_{14}O_7N_5P_2H_2O$ . The mother liquor from the adenine nucleotide yielded the brucine salt of uracil nucleotide.

CHEMICAL ABSTRACTS.

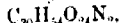
### Carbohydrate Derivatives of the Mucoids and Mucins.

O. SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1920, **87**, 31-47).—The hyaloidin content of the mucoids and the mucins is calculated from the analytical results obtained by other investigators for some of these compounds. In the case of ovomucoid, the author also calculates the hyaloidin from the reduction figures obtained by hydrolysing the compound with hydrochloric acid. The communication contains a theoretical discussion of a series of compounds containing hyaloidin.

S. S. Z.

### Nitrogenous Carbohydrate Compounds of Protein.

O. SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1920, **87**, 1-30).—Nitrogenous products, termed by the author hyaloidin, were obtained as cleavage products from egg-white, ovarian fluid, mucin from pig's stomach, and fibrin. Egg-white was treated with 2-3% potassium hydroxide solution at the ordinary temperature until it dissolved, and then boiled for four to five hours with 10% alkali. After precipitating the protein with acetic acid, the concentrated filtrate was treated by the copper-potassium hydroxide method, and further traces of protein were precipitated with alcohol. The hyaloidin was then obtained from this fraction either by precipitation with lead acetate or by treatment with hydrogen peroxide, and contained copper and chlorine. Hyaloidin prepared from ovarian fluid has the composition  $C_{26}H_{46}O_{20}N_{24}H_2O$ . This hyaloidin and that obtained from *Echinococcus* have the same reducing capacity after boiling with hydrochloric acid. Hyaloidin obtained from egg-white had a similar composition and the same reducing power. Hyaloidin derived from mucin of pig's stomach also shows a reducing capacity of the same order. The author concludes that hyaloidins from the above sources are identical, and suggests that the molecule contains two glucosamine, two hexose, and one acetyl group. Fibrin-hyaloidin obtained from fibrin,



is different from those already discussed, and, in the author's

opinion, contains two glucosamine and three hexose groups, one of which is levulose. The structure of the compound is discussed.

S. S. Z.

**Theory of the Action of Diastase.** GERTRUD WOKER (*Biochem. Zeitsch.*, 1919, **99**, 307—316).—A reply to Wohlgenuth's criticism (*A.*, 1919, i, 361) of the author's theory of the action of diastase.

S. S. Z.

**Formation of the Gum, Levan, by Mould Spores. I. Identification and Estimation. II. Mode of Formation and Influence of Reaction.** NICHOLAS KOPELOFF, LILLIAN KOPELOFF, and C. J. WELCOME (*J. Biol. Chem.*, 1920, **43**, 171—187).—Mould spores (*Aspergillus sydowi*, Bainier) contain an enzyme capable of forming gum in sucrose solutions of all concentrations up to the saturation point. The gum is levan, m. p. about 200°; it yields levulose on hydrolysis, and in the pure condition has  $[\alpha] -40.9^\circ$ . The invertase method may be applied to the estimation of sucrose in the presence of gum. The gum itself may be estimated polariscopically by using a combination of the Clerget and invertase methods.

Levan is formed by levanase from mould spores most readily from "nascent" dextrose and levulose, but it appears that the latter is utilised to a greater extent than the dextrose. Only a slight formation of gum was obtained with reducing sugars in the absence of sucrose. The activity of levanase is influenced by the reaction of the medium. The optimum reaction occurs at about  $pH$  7.0.

J. C. D.

**Preparation of Highly Active Saccharases. III. The Purification of F-preparations by Dialysis.** H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1920, **110**, 175—190).—Several of the authors' saccharase F-preparations were submitted to fractional dialysis through a collodion membrane. It was found that the carbohydrate content of the enzyme increased as the dialysis proceeded until a point was reached at which it became stationary. The authors are therefore of opinion that saccharase must consist chiefly of carbohydrates. On the other hand, the nitrogen content of the dialysed saccharase diminished and reached a limit rather higher than that obtained previously (*Zeitsch. physiol. Chem.*, 1919, **109**, 65). These experiments show that saccharase does not require a co-enzyme for its function. S. S. Z.

**Toxic Actions in Enzymic Processes. I. Inactivation of Saccharase by Heavy Metals.** H. VON EULER and OLOF SVANBERG (*Fermentforsch.*, 1920, **3**, 330—393; from *Chem. Zentr.*, 1920, ii, 200—201).—The experiments were performed by observing the conversion of sucrose by the saccharase solution used previously (*Zeitsch. physiol. Chem.*, 1919, **107**, 273). It is found that the toxic power of the silver ion towards saccharase is considerably

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greater than that of the mercuric ion. The enzyme is thereby inactivated, but not destroyed, since its power is completely restored by removal of the heavy metal or by converting it into an insoluble form (by hydrogen sulphide). The graph showing the relationship between toxicity and concentration in the case of mercuric chloride resembles the dissociation curve, whereas complete proportionality is found in the case of silver nitrate. The substrate (sucrose) exercises a considerable protective action towards metallic poisoning, which must be taken into account in calculating the necessary amount of poison per enzyme unit. With small amounts of mercuric chloride, the coefficient of inversion falls rapidly with the time. The degree of poisoning also depends on the length of time during which the mercuric chloride and saccharase are in contact previous to inversion; "self-regeneration" of the enzyme occurs gradually, the process appearing to be analogous to the "Danysz" effect in immunochemistry. The concentration of free silver ions becomes greatly diminished after addition of the enzyme solution to a dilute solution of silver nitrate, but metallic or colloidal silver is not formed, so that it would appear that union occurs with some components of the enzyme solution; it is found by electrometric measurement that each c.c. of enzyme solution (containing 56 mg. of dry substance) requires from 28 to 55 mg. of silver. The toxic action of auric chloride towards saccharase is of the same order as that of mercuric chloride, whilst copper sulphate is much less poisonous, and cadmium sulphate, thallium sulphate, and uranium nitrate are scarcely toxic.

The previous data concerning the inhibition of enzyme actions by heavy metals are collected.

H. W.

**Artificial Zymogens.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1920, 104, 316—322).—The name artificial zymogen is given to enzymes inactivated by nickel or by mercuric chloride, this inactivation being assumed to be due to the formation of complex compounds of the enzyme with the inactivating substance.

Inactivation of urease is effected by means of minimal proportions of nickelous oxide, whereas a somewhat large quantity of the undissolved metal is required for the same purpose; it is now found that only the slight traces of metal passing into solution are active in this respect. In order to decide whether the nickel combines with the enzyme molecules or whether the metal in the free state in solution prevents the enzymic action, inactivated urease solution was subjected to dialysis, its action on carbamide being then examined both before and after activation by means of potassium cyanide. It is found that the zymogen is not activated by dialysis alone, but remains in the dialysed solution. The conclusion is drawn that the nickel forms an actual compound with the enzyme. Experiments made in presence of glycine indicate that the nickel enters the amino-acid compound, thus leaving the zymogen and escaping dialysis; in this way, the enzyme is rendered active.

T. H. P.

**Preparation of o-Guätholmonomethyltrioxyarsenomenthol.**

ALFRED MAUERSBERGER (D.R.-P. 320797; from *Chem. Zentr.*, 1920, iv, 293).—(i) Mentholguätholsulphuric ester is condensed with disodium monomethyl arsenate. (ii) Sodium benzenedisulphonate is treated with sodium ethoxide, and subsequently with sodium arsenite; the intermediate product so obtained is treated with methyl menthylsulphate. Mentholguätholsulphuric ester is a brown, oily liquid. The final product is a viscous mass, which solidifies at about 22° and has b. p. 154° (decomp.); it is expected to find application in pharmacy.

H. W.

**Synthesis of Boranilides. I. Boranilide and its Derivatives.** TARINI CHARAN CHAUDHURI (T., 1920, 117, 1081—1086).**Elements of the Oxygen Group and Organo-magnesium Compounds.** M. GIUA and F. CHERCHI (*Gazzetta*, 1920, 50, i, 362—377).

—The action of tellurium on magnesium phenyl bromide is similar to that of sulphur or selenium, and results in the formation of phenyl telluromercaptan, diphenyl ditelluride, phenyl telluride, and, in small proportion, hydrogen telluride: (1)  $\text{MgPhBr} + \text{Te} = \text{Ph} \cdot \text{Te} \cdot \text{MgBr}$ , and the latter  $+ \text{HCl} = \text{MgClBr} + \text{TePhH}$ ; (2)  $2\text{MgPhBr} + 2\text{Te} = \text{TePh}_2 + \text{Te}(\text{MgBr})_2$ , and the latter  $+ 2\text{HCl} = \text{TeH}_2 + 2\text{MgClBr}$ . The amount of hydrogen telluride indicated by equation (2) is, however, greater than that actually formed when the complex is treated with dilute acid. The formation of phenyl telluride appears to be due to decomposition of the phenyl telluromercaptan, as this readily undergoes oxidation to diphenyl ditelluride, which decomposes into tellurium and phenyl telluride.

The action of sulphur, selenium, or tellurium on magnesium pyrrol iodide yields black, infusible compounds which, from their properties, are pyrrole-blacks containing, respectively, sulphur, selenium, and tellurium (compare Angeli and Pieroni, A., 1919, i, 134). These results indicate the complete chemical analogy existing between tellurium and the other elements of Group VI of the periodic system. The possible existence of isotopes in the case of tellurium is discussed.

Phenyl telluromercaptan,  $\text{PhTeH}$ , is unstable, but with mercuric chloride forms the compound,  $\text{TePh} \cdot \text{HgCl}$  (compare Lederer, A., 1915, i, 1056), m. p. 85—90° (decomp.); it yields also a grey auriferous chloride, m. p. 154—156°, and a yellow, amorphous platinumchloride, i. p. 75—80°.

The products obtained by the action of tellurium on magnesium phenyl bromide were fractionated at a pressure of 85 mm. When treated with concentrated sulphuric and nitric acids, the fraction having b. p. 155—200° yields a pale yellow, amorphous substance  $\{(\text{NO}_2 \cdot \text{C}_6\text{H}_4)_2\text{TeO}\}$ , which contains 6.4% N and does not melt at 250°.

The residue failing to distil at 200° gives, when treated with concentrated nitric acid, (1) phenyltelluric acid nitrate,  $\text{C}_6\text{H}_5\text{O}_4\text{NTe}$ , m. p. 210—212° (Lederer, *loc. cit.*, gave m. p.

232°–233°); the latter is decomposed by sodium hydroxide, giving the compound,  $O(TePh_3 \cdot NO_3)_2$ , m. p. 223°–224° (compare Lederer, *loc. cit.*). (2) A compound which separates in minute, shining, white crystals, m. p. 66°–68°, and at a higher temperature becomes solid, and then has m. p. 201°–203° (decomp.); this compound loses 2.89% at 80°–90°, the formula  $O \cdot TePh \cdot NO_3 \cdot 2EtOH$ , corresponding with 2.46% of alcohol, and  $Te_2O_7 \cdot N_2Ph_4 \cdot 6EtOH$  with 2.82%.

The same fraction (above 200°) reacts energetically with bromine in ethereal solution, giving the compound,  $Te_2Br_4Ph_2$ , which forms shining, yellow crystals, m. p. 200°, becoming opaque in the air and loses part of its bromine when treated with alkali carbonate or hydroxide.

Analysis of the black compound resulting from the action of sulphur on magnesium pyrrol iodide gave: N 13.06–13.37, S 21.67, and ash 0.205%.

T. H. P.

## Physiological Chemistry.

**Relative Value of Fat and Carbohydrate as Sources of Muscular Energy. With Appendices on the Correlation between Standard Metabolism and the Respiratory Quotient during Rest and Work.** AUGUST KROGH and JOHANNES LINDBHARD [with GÖRAN LILJESTRAND and KNUD GAD ANDERSEN] (*Biochem. J.*, 1920, **14**, 290–361).—An elaborate and valuable study of this important question. A method of determining the respiratory exchange of human subjects is described which admits of a high degree of accuracy. All the results agree in showing that work is more economically performed on carbohydrate than on fat. A hypothesis regarding the physiological utilisation of fat and carbohydrate during work is advanced.

J. C. D.

**Habituation to Bromine Vapour and Action of the Latter on the Blood.** S. MARINO (*Arch. farm. sper. sci. aff.*, 1920, **29**, 48–61).—Respiration of bromine vapour causes diminution of the number of red corpuscles and of the content of haemoglobin in the blood. The extent of this diminution increases with the quantity of the vapour administered, but not with repetition of the treatment. Habituation of the animal organism to bromine vapour is attainable by gradual increase of the dose, but even continued small doses produce haemolysis. The vapour conditions marked increase in the leucocytes, sometimes to about four times their normal number.

T. H. P.

**Injurious Action of Carbon Dioxide on Red Blood Corpuscles.** W. PATZSCHKE (*Zeitsch. physiol. Chem.*, 1920, **109**, 1–11).—Experiments in vitro show that carbon dioxide increases

by fifty or one hundred times the action of inorganic blood poisons which form methæmoglobin, the incidence of the reaction being accelerated markedly by rise of temperature. In presence of aniline or nitrobenzene, the formation of methæmoglobin in human blood occurs only after introduction of carbon dioxide. It is therefore probable that the development of the action of certain poisons in the veins is brought about by the carbon dioxide present. Intensification of the formation of methæmoglobin by carbon dioxide is produced, not only in suspensions, but also in solutions of blood corpuscles and in hæmoglobin solutions, so that it may be assumed that the carbon dioxide induces changes in the hæmoglobin favourable to the formation of methæmoglobin. Blood corpuscles charged with carbon dioxide are labile cells readily accessible to injury, whereas oxygen protects the corpuscles.

T. H. P.

**Antigens and Serological Specificity. XIV. Specific Serum Reactions with Simple Compounds of Known Constitution (Organic Acids).** KARL LANDSTEINER (*Biochem. Zeitsch.*, 1920, 104, 280—299. Compare this vol., i, 260).—The experiments now described show that with diazotised aniline-*m*-sulphonic acid, *p*-arsanilic acid, *o*-toluidine-5-sulphonic acid coupled with tyrosine, *m*-hydroxybenzoic acid, and salicylic acid the precipitin reactions of the corresponding azo-proteins are completely or almost completely destroyed; the action is a specific one, the specificity resembling that of the precipitin reactions of the azo-proteins themselves. Not only are the precipitations prevented by these azo-compounds, but with the help of the latter the precipitates, when formed, may, after centrifugation and washing, be dissolved. These inhibiting substances contain a group identical with the specific group of the corresponding azo-protein with which the immune serum employed reacts. The assumption may therefore be made that the inhibiting body combines with the anti-substance of the immune serum, and so prevents this from acting on and precipitating the azo-protein present in the solution. Such specific serum reactions with synthetic compounds of known constitution represent a new discovery.

Experiments have been made with simpler compounds in the same way as with the azo-colouring matters. As regards the azo-components corresponding with the immune sera, sodium *m*-aminobenzenesulphonate and *p*-aminophenylarsinate in neutral solution exhibit selective inhibiting action. In equimolecular proportions, the azo-colouring matters act considerably more strongly than the simple amino-acids, although these act at moderately low concentrations. The connexion between inhibiting effect and chemical constitution has further been investigated with a large number of other compounds, such as amino-acids and carboxylic, sulphonic, and arsenic acids free from amino-groups.

Of the various monobasic, polybasic, saturated, unsaturated, and substituted aliphatic carboxylic acids, most produce no, and none marked, inhibition of the precipitin reaction with the immune sera. With the aromatic and cyclic carboxylic acids, the action depends

on the constitution. The results obtained with benzene derivatives depend less on the character of the substituents than on their position, although the carboxyl group has a somewhat greater influence than other substituent groups. The results obtained are given in detail and discussed.

T. H. P.

**Formation of Protein from Carbamide by Ruminants.**

E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 276—279).—

As regards the source of the sulphur of the protein formed in sheep fed with straw previously treated with sodium hydroxide (this vol., i, 699), it appears that the sheep were supplied with various inorganic salts, including potassium sulphate and sulphide. Estimation of the sulphur in the ash of straw treated with sodium hydroxide according to Beckmann's method shows that it is only just sufficient, if completely utilisable, to furnish the sulphur of the flesh formed by the sheep during the experiment; if the organically bound sulphur of the straw is included, more than sufficient sulphur is supplied. The source of the tryptophan still remains an open question.

T. H. P.

**Taurine from Herring Flesh and its Crystallographic Investigation.**

E. BERNER (*Zeitsch. physiol. Chem.*, 1920, **110**, 172—174).—The author has separated about 0.003% of taurine from the flesh of the herring (*Clupea harengus*), and has obtained it in exceptionally well-developed crystals belonging to the prismatic class of the monoclinic system:  $a:b:c = 0.6817:1:0.9073$ ,  $\beta = 93^{\circ}47'$ .

T. H. P.

**Formation of Oxalic Acid in the Animal Body.**

LUDWIG PINCUSSEHN (*Biochem. Zeitsch.*, 1919, **99**, 276—297).—Nucleic acid, xanthine, guanine, uric acid, and allantoin when introduced into the system of dogs and rabbits, either per os or by intravenous injection, produce an increase in the content of oxalic acid and a decrease in the allantoin content of the urine. The uric acid remains constant. Similar observations were made in a more pronounced way when the substances were previously "sensitised" and exposed to light.

S. S. Z.

**Amino-acid Synthesis in the Animal Organism. Can Norleucine Replace Lysine for the Nutritive Requirements of the White Rat?**

HOWARD B. LEWIS and LUCIE E. ROOR (*J. Biol. Chem.*, 1920, **43**, 79—87).—Eighteen per cent. of gliadin as the sole source of protein in the diet of a young rat will not permit growth until the inadequacy of lysine is made good. Neither *dl*-norleucine nor *d*-norleucine is able to supply the deficiency of a gliadin diet as does a supplement of lysine.

J. C. D.

**Relation of Urochrome to the Protein of the Diet.**

K. F. PELKAN (*J. Biol. Chem.*, 1920, **43**, 237—242).—The excretion of

urochrome appears to be dependent on the amount of protein in the diet.

A substance, protochrome, which gives similar reactions to urochrome, can be produced from certain proteins. All evidence points to the fact that urochrome, lactochrome, and protochrome are identical, and, at least to a large extent, are derived from the food proteins.

J. C. D.

**Presence of Iodine in Large Quantities of Sheep Pituitary Glands.** EMILY C. SEAMAN (*J. Biol. Chem.*, 1920, **43**, 1-2).—No iodine was detected in quantities of sheep pituitary gland as large as 100 grams (compare Denis, A., 1911, ii, 746).

J. C. D.

**Decomposition Products of Atractylin in the Animal Organism.** A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 88-96).—In an alkaline medium, atractylin, which has the probable formula  $C_{30}H_{52}O_{15}S_2K_2$ , decomposes, yielding sulphuric and valeric acids, a carbohydrate, and a complex product (A), which is obtained as a white powder, and gives the following reactions: in concentrated sulphuric acid containing traces of formaldehyde it dissolves to a red solution, which is turned deep blue by addition of a small quantity of water; with concentrated sulphuric acid and a few drops of aqueous vanillin solution, it yields an intense carmine-red coloration. By means of these reactions, the gastro-intestinal contents and various organs of a dog poisoned with atractylin were shown to contain this product A.

T. H. P.

**Relation of Hyaloidin to the Formation of Chondroitin-sulphuric Acid, Collagen, and Amyloid in the Organism.** O. SCHMIEDEBERG (*Arch. exp. Path. Pharm.*, 1920, **87**, 47-74).—A theoretical paper containing a critical discussion of the above subject.

S. S. Z.

**The Existence in the Bile of an Inhibitor for Hepatic Esterase, and its Nature.** GEORGE MACFEAT WISHART (*Biochem. J.*, 1920, **14**, 406-417).—An inhibitory substance for the esterase of liver was found to be present in the bile of all the animals examined. It is probably the cholic acid portion of the bile acid molecules which is responsible for the effect.

J. C. D.

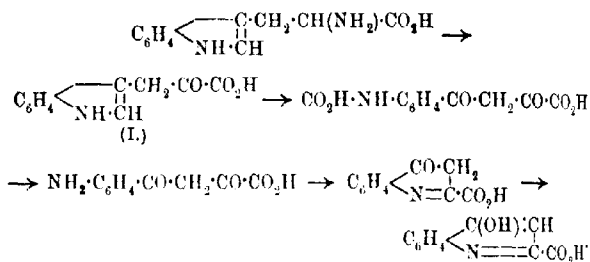
**Bioluminescence. I. The Luciferin and Luciferase of *Cypridina hilgendorffii*. II. The Production of Light by *Cypridina hilgendorffii* is not an Oxidation.** S. KANDA (*Amer. J. Physiol.*, 1920, **50**, 244-260, 561-573).—I. Two substances, corresponding with luciferin and luciferase found by Dubois in *Pholas dactylus*, are concerned in the production of light by *Cypridina hilgendorffii*. The first is thermostable; the second is destroyed by heat. Both are produced only in the maxillary gland cells of the animal. The author is of opinion that Harvey's theory and nomenclature (A., 1917, i, 365) are not tenable. II. The



intensity of light produced by *Cypridina* in recently boiled water saturated with various gases was strongest in hydrogen and weakest in oxygen. Saturation with carbon monoxide, carbon dioxide, or nitrogen gave lights of intermediate intensities. It is concluded that the light cannot be produced by oxidation.

## CHEMICAL ABSTRACTS.

**Formation of Kynurenic Acid from Tryptophan in the Animal Body.** A. ELLINGER and Z. MATSUOKA (*Zeitsch. physiol. Chem.*, 1920, **109**, 259—271. Compare A., 1914, i, 865).—The authors have synthesised indolepyruvic acid, and find that, when this acid is administered subcutaneously as sodium salt to a dog, it is possible to isolate from the urine kynurenic acid in amount rather less than one-half of that obtained when tryptophan is injected. The conclusion is drawn that the conversion of tryptophan into kynurenic acid is best represented by the scheme (compare Dakin, "Oxidations and Reductions in the Animal Body," 1912, 73; Barger and Ewins, A., 1917, i, 476):



The condensation of indole-3-aldehyde and hippuric acid in presence of acetic anhydride and sodium acetate yields, not the azlactone (compare Ellinger and Flamand, A., 1908, i, 372), but its 1-acetyl derivative (annexed formula), which crystallises in pale yellow rhombic or oblique rhombic plates, m. p. 205—206°, and, when treated with sodium hydroxide solution, yields

*Indolepyruvic acid* (formula I, above), which forms yellow (+ C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) or almost colourless crystals. Its *p*-nitrophenylhydrazone, C<sub>12</sub>H<sub>6</sub>N·CH<sub>2</sub>·C(CO<sub>2</sub>H)N·NH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, crystallises in rosettes of yellow plates, m. p. 153—154°.

When quinoline-2-carboxylic acid is administered as sodium salt subcutaneously to a dog, it is separated in the urine partly unchanged and partly coupled with glycine, but does not undergo oxidation to kynurenic acid.

T. H. P.

**Behaviour of Aspirin in the Animal Organism.** A. PITINI (*Arch. Farm. sper. Sci. aff.*, 1920, **29**, 113—118).—Investigation

of the urine of dogs to which aspirin had been administered indicates the presence of unchanged aspirin, so that part of the aspirin is absorbed in the animal organism before undergoing hydrolysis.

T. H. P.

**Appearance of Acetaldehyde in the Body due to Cleavage of Ethyl Alcohol.** WILHELM STEPP (*Arch. exp. Path. Pharm.*, 1920, **87**, 148—153).—The presence of acetaldehyde was established in the blood and urine of a human subject who had previously consumed ethyl alcohol. In the case of a dog which had received ethyl alcohol, acetaldehyde was found in the urine, but not in the blood.

S. S. Z.

**Chemistry of the Proteins. The Species Specificity of the Structure of Protein.** E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **99**, 204—219).—A theoretical paper in which the structure of protein molecules in relation to immunity and heredity phenomena, and the mechanism of protein synthesis and degradation, are discussed.

S. S. Z.

**Nature of Anaphylaxis.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1920, **109**, 289—297. Compare A., 1912, ii, 1194).—The authors have treated guinea-pigs by subcutaneous or intraperitoneal injection with glycine and its polypeptides up to heptaglycylglycine, but no phenomena were obtained resembling anaphylactic shock, with the exception of slight variations in the temperature. From the heptapeptide onwards, the injection causes a characteristic skin affection.

Methods are described for preparing glycine ethyl ester hydrochloride in large amounts from chloroacetic acid, and pentaglycylglycine from tetraglycylglycine and chloroacetyl chloride.

T. H. P.

**Chemical and Morphological Studies on Cholesterol and its Esters in Normal and Pathological Organs.** JOHAN FAX (*Biochem. Zeitsch.*, 1920, **104**, 82—174).—The author's investigations show that Windaus's digitonin method (A., 1910, ii, 462), as modified by Thaysen (A., 1914, ii, 438), is the only method yet described giving trustworthy results for the estimation of cholesterol in its pure solutions. Preliminary drying in a current of air of the organs from which the cholesterol and its esters are to be extracted is not to be recommended, but treatment of the organs with 2% sodium hydroxide solution and extraction of the alkaline solution with ether result in quantitative extraction and in an extract of such purity that the cholesterol and its esters may be estimated exactly by the above method.

The proportions of free and combined cholesterol in the liver show very slight variations in all the cases examined, including two of cirrhosis of the liver. In the kidneys, of both normal and diseased individuals, the free cholesterol varies but little in amount, and the same holds for the combined cholesterol, even in the cases

of diabetes, pernicious anæmia, cirrhosis of the liver, and sepsis examined; with diseases of the kidneys, however, the normal small proportion of cholesterol present as ether is considerably exceeded. Inconsiderable variations occur in the proportion of free cholesterol in the suprarenal glands, but the combined cholesterol exhibits wide differences in different cases, the highest amounts being found in two instances of kidney disease and in one normal instance. In no case examined was cholesterol detectable morphologically in the liver, but with kidney disease of long standing the ester of cholesterol may be discovered morphologically in the kidneys in amount corresponding well with that found chemically.

T. H. P.

**The Colloid Chemical Importance of Physiological Ionic Antagonism and of Equilibrated Salt Solutions.** S. M. NEUSCHLOSZ (*Pflüger's Archiv*, 1920, 181, 17—39; from *Chem. Zentr.*, 1920, iii, 312).—It has not been well established that the physiological action of ions depends solely on their relationship to the proteins, and that these relationships are purely chemical in character. In many physiological phenomena, in the cell, lipoids play a predominating rôle. Solutions of lecithin (2%) have been treated with equal quantities of salt solutions and their surface tensions determined stalagmometrically. The chlorides of the cations Na, K, Ca, Mg, and Al noticeably increase the surface tension of lecithin solutions. With mixtures of these salts, an antagonism between the cations is very obvious. The surface tension of a lecithin solution in the presence of a mixture of salts is dependent, in the first place, on the relative ratio of concentration of the cations, and is not influenced within wide limits by the absolute concentration of the solution. A far-reaching parallelism exists between physiological and colloidal chemical ionic antagonism as shown in this manner. The physico-chemical basis of ionic antagonism is found in the capacity shown by the cations of mutual replacement from their adsorption compounds (in this case from the surface of the lecithin particles), but the displacing ion does not take the place of that displaced.

H. W.

**Water-soluble Vitamines. I. Are the Antineuritic and the Growth-promoting Water-soluble-B Vitamines the Same?** A. D. EMMETT and G. O. LUCAS (*J. Biol. Chem.*, 1920, 43, 265—286).—Experiments designed to ascertain whether these two substances are identical lead the authors to suggest, tentatively, at least, that they are not the same. The antineuritic factor appears to be more readily decomposed by heat. The lack of strictly quantitative methods renders the conclusion indefinite.

J. C. D.

**Toxic Action of Cyanogen Chloride.** C. I. REED (*J. Pharm. Expt. Ther.*, 1920, 15, 301—304).—This action is primarily due

to the formation of hydrocyanic acid, but in delayed poisoning the chlorine may also have an effect. Protection may be given by sodium thiosulphate. J. C. D.

## Chemistry of Vegetable Physiology and Agriculture.

**Control of the Purity of Preparations of Carbohydrate by Bacterial Fermentation Tests.** H. O. SCHMIT-JENSEN (*Compt. rend. Soc. Biol.*, 1920, **83**, 699—701; from *Chem. Zentr.*, 1920, iv, 217).—Different types of bacteria can be investigated by their action towards different carbohydrates (*Compt. rend. Soc. Biol.*, 1920, **83**, 502); conversely, the purity of carbohydrates and polyhydric alcohols can be tested by fermentative action if the necessary classes of bacteria are available. H. W.

**Proteins of Putrefactive Bacteria.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, **109**, 49—56).—Putrefactive bacteria are found to contain two protein compounds, one having the characters of the albumoses and the other those of a globulin-like protein. Neither contains the tryptophan group, whilst the atomic complex giving the xanthoprotein reaction is almost entirely lacking with the albumose and present in extremely small proportion in the protein. When heated in a narrow test-tube, both emit vapour capable of blackening lead acetate paper (Siegfried's reaction), whereas this behaviour is not shown by the proteins and is doubtful with the albumoses.

Since Siegfried's reaction was unknown to Nencki, it is possible that the latter's anthraxprotein (A., 1885, 178) is not quite free from sulphur. Further work is necessary to ascertain if unicellular organisms are able to produce proteins not lacking in cyclic and heterocyclic groups, but possibly this power is restricted to the true plants, among which bacteria and yeasts cannot be placed. Between plants and animals lies a third group of organisms, which are able to utilise inorganic nitrogen to build up their body-substance, but are unable, apparently owing to absence of chlorophyll, to convert inorganic into organic carbon.

Voeltz (*Berlin Klin. Woch.*, 1919, No. 29) fed sheep for seventeen to twenty-five days solely on straw (treated with sodium hydroxide and free from digestible nitrogen), sugar, starch, and carbamide, growth and accumulation of protein taking place. The sources of the sulphur and the tryptophan group of the protein formed are obscure. T. H. P.

**The Enzymes of *B. Coli communis* which are Concerned in the Decomposition of Dextrose and Mannitol. IV. The Fermentation of Dextrose in the Presence of Formic Acid.** EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1920, [B], **91**, 294—305).—The products obtained in the decomposition of dextrose by

*Bacillus coli communis* are divided into three groups: (1) lactic acid; (2) acetic acid, alcohol, and succinic acid; (3) formic acid, carbon dioxide, and hydrogen, there being a closer relationship between the products of groups (2) and (3) than exists between either group and group (1). The proportions in which the products of group (2) appear depend on the intimacy with which the reactions of this group co-operate with the reactions of group (3), and this further explains the fact that in many normal fermentations there is a tendency for groups (2) and (3) to appear as constituting one group.

It is now demonstrated that hydrogen, nascent during the fermentation, does take part in the production of alcohol, the hydrogen arising either from the decomposition of the dextrose itself or from the simultaneous fermentation of added calcium formate. It is also shown that the presence of calcium formate does not depress the formation of formic acid, and the consequent yield of its gaseous products, carbon dioxide and hydrogen, in the fermentation of dextrose by *B. coli communis*.

W. G.

**Action of *Bacillus fluorescens liquefaciens* (Flügge) on Asparagine in a Definite Chemical Medium. II. Products from, and Mode of Attack on, Asparagine.** A. BLANCHETIERRE (*Ann. Inst. Pasteur*, 1920, **34**, 392-411).—The chief products formed are acetic, malic, succinic, fumaric, and carbonic acids. The mechanism of their formation is discussed.

J. C. D.

**Influence of the Nature of the Carbonaceous Food on the Utilisation of Nitrogen by *Bacillus subtilis*.** E. ACBEL (*Compt. rend.*, 1920, **171**, 478-480).—Glycerol gives a better yield of culture and a better utilisation of nitrogen than levulose, and this in turn than dextrose, when added to the culture solution of *Bacillus subtilis*. The high yield of organism and increased utilisation of nitrogen with glycerol are probably due to its preliminary conversion into pyruvic acid, and it is noted that sodium pyruvate gives even better results than glycerol.

W. G.

**Experiments on Osmosis and on Aspiration due to Evaporation, Suitable for Use in Plant Physiology.** PIERRE LESAGE (*Compt. rend.*, 1920, **171**, 358-360).—Simple modifications of the experiments of Dutrochet and Askenasy are described.

W. G.

**Fluorescence and Condition of Chlorophyll in Living Cells.** KURT STERN (*Ber. Deut. Bot. Ges.*, 1920, **38**, 28-35).—The author's spectroscopic investigations show that chlorophyll fluoresces only in true solution, colloidal chlorophyll solutions and solid chlorophyll exhibiting no appreciable fluorescence. Observation of the fluorescence of turbid media with the naked eye leads to erroneous conclusions, spectroscopic examination being necessary to ascertain the real strength of the fluorescence. In the intact cell, the chlorophyll is contained in lipoidal, true, and fluorescing

solution. The process of assimilation proceeds partly in the lipoidal and partly in the hydroid phase, and surface-active substances alter the limiting surface between the two phases and thereby retard or assist assimilation.

T. H. P.

### Behaviour of certain Organic Compounds in Plants. XII.

G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1920, 50, ii, 13—46).—An account of work already published (A., 1919, i, 58, 140, 241; his vol., i, 408).

T. H. P.

### Enzyme Formation with *Aspergillus niger*. H. von

EULER and S. ASARNOJ (*Fermentforsch.*, 1920, 3, 318—329; from *Chem. Zentr.*, 1920, iii, 201—202).—The investigation proceeded along lines similar to those adopted by Euler and Svanberg (A., 1919, i, 201, 614) in the case of saccharase in bottom yeast. As far as saccharase is concerned, it is found that the total enzyme action remains almost unchanged if the well-ground fungus material is brought into contact with sucrose solution either after being warmed to a temperature at which the saccharase is not damaged or after being dried with or without toluene. Wohlgenuth's method can only be applied with difficulty to the estimation of amylase by the direct action of the fungus material on starch solution; the sugar which is formed is best estimated by Bertrand's reduction method. For the type investigated, and under certain conditions, the inverting capacity,  $I_t = k \times g$  sugar/g dry substance, is found to be  $0.32 \times 10^{-2}$ . A fungus which had been grown on starch solution with the addition of peptone had a saccharase activity about 30% higher than that of a specimen grown under similar conditions but in the absence of peptone. Addition of peptone to the nutrient solution, which otherwise contains only inorganic nitrogen, also influences the formation of amylase. The data of other workers with regard to the improvement in the formation of amylase, due to addition of starch to the nutrient solution, could be quantitatively confirmed.

H. W.

### Water-soluble Vitamines. II. The Relation of the Antineuritic and Water-soluble Vitamines to the Yeast Growth-promoting Stimulus. A. D. ENNETT and MABEL STOCKHOLM (*J. Biol. Chem.*, 1920, 43, 287—294).—Further

evidence is given in support of the theory that the antineuritic and the growth-promoting vitamines are not identical. It is also possible that the substance which promotes cell-division in yeast is another factor of the vitaminic type. It is therefore considered inadvisable to employ the quantitative method introduced by Williams (A., 1919, i, 463) until the differentiation of these factors has been satisfactorily accomplished.

J. C. D.

### Comparative Studies on Respiration. XI. Effect of Hydrogen-ion Concentration on the Respiration of *Penicillium chrysogenum*. F. G. GUSTAFSON (*J. gen. Physiol.*, 1920, 2, 617—626).—Variations in the $P_H$ value between 4 and 8

produce practically no effect on the normal rate of respiration of *Penicillium chrysogenum* (the rate at neutrality is considered normal). Increasing the  $P_H$  value to 8.80 causes respiration to fall to 60% of the normal, after which it remains stationary for the duration of the experiment. Decreasing the  $P_H$  value to 2.65 causes a gradual rise and a gradual return to the normal; at  $P_H$  1.10 to 1.95 the preliminary rise amounts to 20%, and is followed by a fall to below the normal. The decreases in respiration brought about by solutions of a  $P_H$  value of 1.95 or less are irreversible, whilst a similar decrease which occurs at  $P_H$  8.80 is reversible, the rate coming back to practically normal after the material is replaced in a neutral solution.

Determinations by means of Winkler's method showed an increase in the consumption of oxygen in acid solutions and a decrease in alkaline solutions.

H. W.

**Crystallisable Sugar and Free Acids in Plants.** H. COLIN (*Compt. rend.*, 1920, 171, 316--318). The fact that sucrose exists in a large number of fruits in the presence of free acid at a concentration more than sufficient to cause its inversion is shown to be due to the presence of alkali salts of the organic acids in the juices, which lessen the hydrolysing action of the free acids.

W. G.

**Relation between the Calcium and the Nitrogen Content of Plants and the Function of Calcium.** F. W. PARKER and E. TRUOG (*Soil Sci.*, 1920, 10, 49--56).—From the consideration of a large number of analyses of various plants with respect to their nitrogen, phosphorus, potassium, calcium and magnesium content, it was observed that the only element the amount of which was closely related to the nitrogen content was calcium. These plants could be grouped in two classes, according to their calcium-nitrogen ratio. In one group the ratio was low, averaging 0.306, and this group consisted of plants of the grass family, which have a low lime requirement. In the other group the ratio was high, 0.553, and the group contained the legumes and other plants which have a high lime requirement and are sensitive to soil acidity. These results point to the conclusion that plants which have a high nitrogen or protein content, and therefore produce a large amount of acidity from protein metabolism, require a large amount of calcium as carbonate for the neutralisation of the plant acids.

J. H. J.

**Inulin in the Globe Artichoke.** RUTH OKEY and ANNA W. WILLIAMS (*J. Amer. Chem. Soc.*, 1920, 42, 1693--1696).—In a sample of globe artichoke which, by the ordinary methods of analysis of foodstuffs, gave 6.8% of nitrogen-free extractives, the authors found 2.5% of inulin and altogether 4.2% of total carbohydrate extracted by water and 1% hydrochloric acid.

W. G.

**Enzyme Action in *Echinodontium tinctorium*,** Ellis and Everhart. HENRY SCHMITZ (*J. gen. Physiol.*, 1920, 2, 613--616).—The present paper is the second of a series dealing with the

physiology of wood-destroying fungi (compare Schmitz and Zeller, *Ann. Missouri Bot. Garden*, 1919, 6, 193). In *Echinodontium tinctorium*, the presence of the following enzymes has been demonstrated: esterase, maltase, lactase, sucrase, raffinase, diastase, inulase, cellulase, hemicellulase, urease, rennet, and catalase.

H. W.

**Carbohydrates of *Lichen islandicus*.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1920, 110, 158—166. Compare A., 1919, i, 242).

—The author confirms the statement of Errera (Diss., 1882) and others to the effect that *Lichen islandicus* contains two carbohydrates: (1) lichenin, which gelatinises when the hot solution is cooled and gives no reaction with iodine, and (2) a soluble carbohydrate which, contrary to the statement of Ulander and Tollens (A., 1906, ii, 193), gives a decided blue coloration when carefully treated with iodine solution; this coloration is, however, distinctly less intense than that obtained with starch, and it is possible that this carbohydrate, known as *isolichenin*, is not a single individual, and that the iodine reaction depends on the presence of a third carbohydrate in small proportion.

The physical constitution of lichenin in the moist state suggests that this compound either belongs to the pectins or contains these. Dry lichenin does not, however, respond to the method for detecting pectin given by von Fellenberg (A., 1916, ii, 351), according to whom the pectins yield methyl alcohol when treated with sodium hydroxide solution.

T. H. P.

**Kinetics of the Action of Catalase Extract from Marine Algae, with a Note on Oxydase.** HAROLD CLARK HAMPTON and

LOURENS G. M. BAAS-BECKING (*J. Gen. Physiol.*, 1920, 2, 635—649).—Preliminary investigations of the catalase, peroxydase, and oxydase of marine algae are described, the present communication dealing only with *Ulva taeniata*, Setchell and Gardner. This contains a catalase, which adheres to the cells to a certain extent, but may, mechanically or by exosmosis, pass into the surrounding medium. This catalase is able to act on peroxide in a neutral medium, the reaction being unimolecular. In an alkaline medium, the catalase decomposes peroxide, following the formula of Schmidt-Nielsen,  $K = \sqrt{a-x} \cdot \sqrt{a-x} / t \sqrt{a(a-x)}$ . The reaction time varies in a linear relation with the concentration of the peroxide. Reaction velocity and enzyme concentration vary in a linear relation. Reaction velocity and peroxide concentration vary in a continuous non-linear and non-exponential relation. Since the peroxide is in excess of the feeble catalase, these facts are in agreement with the data of Senter on blood catalase. On dilution, the enzyme is destroyed, following highly exponential lines,  $dx/dt = K(a-x)^3$ , or even  $dx/dt = K(a-x)^4$ .

*Ulva taeniata* contains oxydase; the presence of peroxydase is not proved.

H. W.



**Extractive Substances of *Melolontha vulgaris*.** DANKWART ACKERMANN (*Zeitsch. Biol.*, 1920, **71**, 193—202).—This organism is found to contain uric acid, leucine, putrescine, lysine, *p*-hydroxyphenylethylamine, choline, and either cholesterol or an allied sterol. Melolonthine (compare Schreiner, A., 1871, **24**, 1201), creatine, creatinine, betaine, and tyrosine could not be detected.

T. H. P.

**Action of Rain Water on the Deposits from Copper Spray Liquids.** G. VILLEDIEU and (MME) VILLEDIEU (*Compt. rend.*, 1920, **171**, 360—363).—Ordinary country rain water does not dissolve even traces of copper from the precipitate obtained in either Bordeaux or Burgundy mixtures.

W. G.

**Acidity of Japanese Acid Clay.** KIURU KOBAYASHI (*J. Chem. Ind. Japan*, 1920, **23**, 543—549).—Japanese acid clay (Japanese fuller's earth) is a closely related mixture of colloidal hydrous aluminium silicates,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and an amorphous anhydrous compound of orthosilicic acid,  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and may be expressed by the formula  $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , where  $x$  is more than 6. The clay itself is not a true acid substance, and the acidity is to be ascribed to its adsorptive property. Adding an acid clay to some basic dye solution, RCl, it may be supposed that the so-called Helmholtz double layer is formed on the surface of the clay, and that it adsorbs hydroxyl ions in accordance with its properties as an acid gel, whilst hydrogen ions are liberated. The radicle R combines with the hydroxyl ions and the hydrogen ions unite with chlorine ions of the basic dye; hydrochloric acid will therefore be liberated. Reaction between an acid clay and neutral potassium chloride solution similarly produces hydrochloric acid, which dissolves aluminium in the clay. The aluminium chloride thus formed will be decomposed by hydrolysis into aluminium hydroxide and hydrochloric acid.

K. K.

**The Occurrence and Nature of the Plant Growth-promoting Substances in various Organic Manurial Composts.** FLORENCE ANNIE MCKERIDGE (*Biochem. J.*, 1920, **14**, 432—450).—The ordinary organic manures used in horticultural and agricultural operations, namely, leaf-mould and fresh and well-rotted stable manure, and well-manured fertile soil, contain, in varying proportions, water-soluble substances, which are effective as plant growth-promoting substances, as is shown by the effect of their aqueous extracts on the development of plants of *Lemna major*. In all cases, the extract of rotted manure was more effective than that of the fresh material. All these materials contain appreciable quantities of nucleic acid and its derivatives in various stages of decomposition, and the greater the bacterial decomposition of the material concerned, the greater is the resolution of the original nucleic acid into its free bases.

W. G.

## General and Physical Chemistry.

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**Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of Very Long Vacuum Tubes.** R. W. WOOD (*Proc. Roy. Soc.*, 1920, [A], 97, 455—470).—The author describes a type of vacuum tube in which it is possible to separate the secondary spectrum of hydrogen from the Balmer series. The tube is 2 m. long and has a 7 mm. bore, and is bent so that the central 40 cm. constitutes an "end on" tube, the electrodes of which are 80 cm. away from the tube. The electrodes are of aluminium; one end of the tube is in permanent connexion with a Gaede pump and the other is connected by a fine capillary tube with a hydrogen generator, either an electrolytic apparatus or a bulb containing palladium and hydrogen. The tube is operated at 25,000 volts and 0.2 ampere. When the pressure is such that there is a Crookes dark space of 4—5 cm., the ends of the tube show a bluish-white light, whilst the central portion shows a fiery purple colour, which exhibits the Balmer spectrum with a secondary spectrum of 1/40th the intensity of that in the side-tubes. It is possible by finer adjustment that the secondary spectrum may vanish entirely. The failure to observe more than twelve members out of the thirty-two emitted by solar hydrogen in the Balmer series is attributed to the numerous lines in the secondary spectrum, which are relatively brighter than the Balmer lines. On photographing the spectrum of the central portion of the tube the author has been able to observe all the Balmer lines up to the 20th. In the region of the 6th to the 14th line each line is practically twice as bright as its succeeding neighbour. This means, if this rate of change is continued, that the 20th line has an intensity of about 1/600,000 that of the  $H_\alpha$  line. A number of other very interesting properties of the long tube are described. The following wavelengths have been measured: 12th line, 3722.12; 13th, 3712.22; 14th, 3703.92; 15th, 3697.35; 16th, 3691.72; 17th, 3686.99; 18th, 3682.96; 19th, 3679.46; 20th, 3676.44, all with reference to Rowland's iron standards. The influence of water vapour on the appearance of the secondary spectrum is described. J. F. S.

**Origin of "Cyanogen" Bands.** S. BARRATT (*Proc. Roy. Soc.*, 1920, [A], 98, 40—49).—Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen. The cyanogen bands are strongly developed in the coal gas-nitrous oxide flame. Evidence is obtained which shows that they are entirely absent from the hydrogen-nitrous oxide flame, if all traces of carbon are excluded, and it appears that carbon is essential to their production. The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any other of the bands

associated with this element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present. The conclusion of Grotrian and Runge, that the cyanogen spectrum is to be attributed to nitrogen, is shown to rest on assumptions which are not confirmed by the present work. The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen admitted in the form of a gas to hydrocarbon flames burning in air, since elementary nitrogen does not appear, in ordinary circumstances, to be effective in producing cyanogen bands in such flames. The intensity of the cyanogen bands, when carbon compounds are admitted to the hydrogen-nitrous oxide flame, bears no simple relation to the amount of carbon thus added.

J. F. S.

**Character of the Light Radiations Emitted by the Vapours of Magnesium, Copper, and Manganese under the Selective Actions of Thermochemical and Thermoelectrical Excitations.** G. A. HEMSALECH (*Phil. Mag.*, 1920, vi, 40, 296—315).—With an electrically heated plate of graphite, which is not covered with a layer of carborundum, the red fringe (this vol., ii, 1, 2, and 170) appears on both sides. The upper fringe often extends to a greater distance from the plate than the lower one, probably on account of convection of vapours expelled from the under surface. The border of the upper fringe is sharply defined and its spectrum emission stops abruptly, in marked contrast to that of the luminous vapour. In the absence of sufficient quantities of ionised vapours strong magnetic fields (1500–2000 C.G.S.) must be applied to displace the red fringe emission appreciably, hence the conclusion previously advanced, that the sharp outline is caused by the magnetic effect of the heating current, is untenable. No satisfactory alternative explanation is offered, but it is pointed out that most luminous phenomena which owe their origin to the flow of an electric current at atmospheric pressure present a sharp outline.

The vapours which fill the protected space are in great part derived from substances on the plate, and the formation of striæ at the boundary surface is interpreted as due to motion of the vapours round the plate in a helical path. The downward drift of luminous vapour in the protected space may be due to gravity or radiation pressure, or their combined action.

An investigation of the spectrum lines emitted by the vapours of magnesium, copper, and manganese showed that the line emission due to thermoelectrical and chemical excitation are of the same type. The characteristic flame lines of magnesium, copper, and manganese, which in the air-coal gas flame are emitted by the mantle above the cone, all appear as long lines in the single plate furnace. This confirms their status as temperature lines.

J. R. P.

**The Fine Structure of the Near Infra-red Absorption Bands of Hydrogen Chloride, Bromide, and Fluoride.** H. M. RANDALL and E. S. IMES (*Physical Rev.*, 1920, 15, 152—155).—Bj

focussing on the slit of an infra-red grating spectrometer the spectrum produced by a prism spectrometer, using a salt prism of small refracting angle, the spectral region to be analysed is too short for the overlapping of spectra. It is possible to employ the full resolving power of a series of graded gratings with the result that in several instances the absorption curves show apparently complete resolution. The position of the narrow absorption bands can be determined with an accuracy of a few Å. In the case of the hydrogen chloride band at  $3.46\ \mu$ , each member of the broad doublet was resolved into twelve narrow bands. From the data obtained, the moment of inertia of the molecules of hydrogen chloride, hydrogen bromide, and hydrogen fluoride is calculated as well as the distance between the atoms in the molecule.

## CHEMICAL ABSTRACTS.

**The Object and Possibility of an Analysis of Absorption**

**Spectra.** I. LIFSCHITZ (*Zeitsch. physikal. Chem.*, 1920, **95**, 1—14, 126. Compare this vol, ii, 208).—A theoretical paper, in which the object of absorption spectrum determination and the possibility of arranging absorption bands in some such series as are found for emission spectra are discussed. The reason for the latter is to remove absorption spectra from a purely empirical study and to find some connexion between the absorption bands and their arrangement and the chromophoric groups of the various substances. The term chromophore is redefined as follows. Chromophores are single atoms or groups of atoms which carry electrons capable of oscillation with frequencies between  $0.3$  and  $1.7 \times 10^{14}$ . J. F. S.

**Optical Effects Occasioned by Salt Formation with Organic Acids. I. Phenols and Enols.** H. LEY (*Zeitsch. physikal. Chem.*, 1920, **94**, 405—442).—The absorption spectra of a number of phenols, phenolic substances, alcohols, and their sodium derivatives have been measured in alcoholic solution by the Hartley method, using an iron arc as the source of light. The following combinations in various concentrations have been measured and recorded: phenol, and sodium phenoxide in ethyl alcohol and in water; *p*-xylenol, *m*-xylenol, thymol, *p*-chlorophenol, *p*-bromophenol, ethyl 2-naphthol-3-carboxylate, *o*-, *m*- and *p*-hydroxycinnamic acids and their ethyl esters, melilotic acid and its ethyl ester, *o*-methoxystilbene, *p*-hydroxystilbene, 2-hydroxydiphenyl, benzoyl-acetic ester, *β*-ethoxycinnamic acid and its ethyl ester, and the sodium derivatives of all the compounds in ethyl-alcoholic solution. Absorption curves have been drawn in all cases, and the changes in the absorption spectra brought about by the salt formation pointed out and considered in the light of the present results and other previously published work. J. F. S.

**Table for the Identification of Dyes by means of the Spectroscope.** JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 9—13).—The position of the centre of the absorption band of a large number of dyes is given, ranging from that of Aurantia at  $\lambda\ 425$  to that of tetramethylthionine at  $\lambda\ 668$ . W. P. S.

**Colour and Chemical Constitution. IV. The Remaining Phthaleins.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 7, 183—188. Compare A., 1917, ii, 349, 557).—Further wave-length measurements of absorption bands are communicated of a number of derivatives, several new, of *pp'*- and of *op'*-phenolphthaleins, and of 4'-hydroxydiphenylphthalide. Quantitative conclusions are derived as to the percentage increase in wave-length of the absorption band of phenolphthalein due to the introduction of various substituents. In agreement with the view previously put forward as to the existence of secondary bands of the phthaleins with a wave-length two-thirds that of the visible band, phenolphthalein and thymolphthalein in alkaline solutions exhibit bands of which the edges are at  $\lambda$  380 and  $\lambda$  420 respectively. The centre of the band for *p*-cresolthymolphthalein in alkaline solution is at  $\lambda$  595, whilst the value calculated from those for phenol-*p*-cresol- and phenolthymolphthaleins is  $\lambda$  597.

By condensation of 5-bromoguaiacol with hydroxybenzoylbenzoic acid, the bromine atom is eliminated and phenolguaiacolphthalein is produced. In this compound, therefore, and presumably also in guaiacolphthalein, it is the methoxy-group which occupies the para-position to the central carbon atom (compare Hindmarsh, Knight and Robinson, T., 1917, 111, 911), and in dibromoguaiacol-phthalein each bromine atom is in the ortho-position to the central carbon atom and also to one hydroxyl group in each nucleus. Quinonoid formulæ are suggested for the salts of quinolphthalein.

J. K.

**Colour and Chemical Constitution. V. The Yellowness of certain Phthaleins when Acid. VI. The Ultra-violet Spectra of the Phthaleins.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 41—44. Compare preceding abstract).—The absorption spectra of phenolsulphonephthalein, of benaurin-*p*-sulphonic acid, and of phenolphthalein monomethyl ether (Green and King, A., 1907, i, 933) only differ from that of benaurin in that the absorption band is moved slightly towards the red owing to the loading of the molecule with the sulphonic and carbomethoxy-groups respectively. Further, since all three compounds are yellow in slightly acid solution whilst phenolphthalein is colourless under these conditions, it is concluded that phenolsulphonephthalein is not a phthalein but benaurin-*o*-sulphonic acid.

Consideration of wave-length measurements by Howe and Gibson (*Physical Rev.*, 1917, 757) of the ultra-violet absorption bands from alkaline solutions of phenolphthalein and its derivatives leads to a modification of the earlier formula (A., 1917, ii, 350) to  $y = \tau - 7$ , indicating that in all phthaleins change of the grouping  $\text{:C} \begin{smallmatrix} \text{O}^- \\ \diagup \\ \text{O} \end{smallmatrix}$  to  $\text{:C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{SO}_3\text{H} \end{smallmatrix}$  is accompanied by a diminution in frequency of 7 units.

J. K.

**Colour and Chemical Constitution. VII. Spectra of Solid Compounds of Cobalt, Nickel, Manganese, and Uranium.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 45—49. Compare preceding abstracts).—Evidence is adduced to show that the effect on the absorption spectrum of loading the molecule either internally by substitution or by combination with a non-ionising solvent noted in the case of certain organic compounds may also be observed among cobalt, nickel, and uranyl salts and among permanganates. It is noted that the wave-lengths of homologous lines of cobalt compounds, of uranyl compounds, and of the phthaleins are respectively proportional to the eighth, sixth, and fourth roots of the molecular weights of the compounds compared.

J. K.

**Colour and Chemical Constitution. IX. An Empirical Law of Change of Colour.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1920, 8, 225—228. Compare preceding abstracts).—An examination of the absorption spectra of the haloid derivatives of phenolphthalein and fluorescein has shown that the effect of the substituents on the position of the bands is given by the relation  $\frac{n}{n_0} = 1 - \frac{m}{100} (1.15 + 0.0037N)$ , in which  $n$  = the frequency for the halogen derivative,  $n_0$  for that of the parent substance (18.05 for phenolphthalein and 20.27 for fluorescein),  $m$  = the number of substituent halogen atoms, and  $N$  = the atomic number of the halogen. The relationship also appears to hold approximately for alkyl derivatives. The view previously advanced that molecular volume is the main factor in colour change is abandoned in view of the fact that the introduction of methyl, isopropyl, chlorine, bromine, and iodine into the molecule produces about the same effect in each case.

J. K.

**Colour and Chemical Constitution. VIII. Fluorescence and its Laws.** JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1919, 8, 51—53. Compare preceding abstract).—The emission spectra of the green fluorescences exhibited by uranyl compounds in the solid condition or in non-aqueous solution have been examined. The bands are equally spaced and probably always five in number, but usually some are too faint to be observed. It is found that for all of them  $\frac{A_n}{A_1} = \left(\frac{F_n}{F_1}\right)^2$ , in which  $A_n$  and  $F_n$  are corresponding wave-lengths in the absorption and fluorescent spectra, and  $A_1$  and  $F_1$  are the respective wave-lengths of the lowest bands in each. The relation also appears to hold for some organic compounds, which give much the same value, 1.15, for the ratio  $\frac{A_n}{A_1}$ .

J. K.

**Scattering of Light by Dust-free Liquids.** W. H. MARTIN (*J. Physical Chem.*, 1920, 24, 478—492).—Dust-free liquids were prepared (i) by evaporation and condensation in an enclosed

exhausted apparatus, (ii) by precipitating gelatinous hydroxides of aluminium, cadmium, and zinc from dilute solutions of the sulphates, and (iii) by cataphoresis of water. The dust-free liquids were all found to scatter light, that of short wave-length being scattered to a much greater extent than that of long wave-length. A relationship,  $(\mu - 1)^2/n$ , formulated by Rayleigh and verified in the case of gases by Strutt, connecting the refractive index of the medium and its light-scattering power, showed some agreement in the case of the liquids investigated. The scattered light is very largely plane polarised in the case of liquids which scatter very little light, and the polarisation in different liquids decreases as the relative intensity of the scattered light increases. The polarisation is much less complete for liquids than for gases. Evidence is given to show that the phenomena observed are due to scattering and not to fluorescence. The following intensities of the scattered light are given in terms of that of toluene = 1: water, 0.060; sulphur dioxide, 0.400; methyl alcohol, 0.160; ethyl alcohol, 0.180; ethyl ether, 0.236; ethyl acetate, 0.210; isobutyl chloride, 0.375; heptane, 0.374; isobutyl butyrate, 0.320; benzene, 0.91; toluene, 1.00; chlorobenzene, 1.52; ethyl benzoate, 1.55; and  $\alpha$ -chloronaphthalene, 4.30.

J. F. S.

**Re-examination of the Light Scattered by Gases in respect of Polarisation. I. Experiments on the Common Gases.**

LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [A], **97**, 435—450. Compare A., 1919, ii, 5).—An improved method by which the residual defect of polarisation in the light scattered by dust-free gases may be measured is described. This quantity has been ascertained for the commoner gases, and the following values of the intensity of weak component polarisation obtained: hydrogen, 3.83; nitrogen, 4.06; air, 5.0; oxygen, 9.4; carbon dioxide, 11.7; nitrous oxide, 15.4 (strong component = 100). The author is of the opinion that the error attached to these values is not greater than 5%, and is probably much less.

J. F. S.

**Re-examination of the Light Scattered by Gases in respect of Polarisation. II. Experiments on Helium and Argon.**

LORD RAYLEIGH (*Proc. Roy. Soc.*, 1920, [A], **98**, 57—64. Compare preceding abstract).—The experiments previously described (*loc. cit.*) are continued for helium and argon. Since the scattering due to helium is so slight, special precautions were taken to ensure the purity of this gas, which consisted in allowing the gas to circulate through a layer of charcoal cooled by liquid air immediately before entering the experimental tube. The intensity of the weak component polarisation is found to be argon 0.46, helium < 6.5 (strong component = 100). The total intensities of light scattered by helium and by air have been compared. The ratio found was 0.0170. Considering the difficulty of the experiment, this is considered to agree within the limit of error with the ratio of the squares of the refractivities, which is 0.0144.

J. F. S.

**Influence of Ammonium Molybdate on the Rotatory Power of Malic Acid.** E. DARMOIS (*Compt. rend.*, 1920, 171, 348—350).—The rotatory power of solutions of malic acid is increased by the addition of ammonium molybdate (compare Gernez, A., 1889, 1147), and the values of  $\alpha_D$  are found to increase at first with the weight of ammonium molybdate and then to become practically constant. If it is assumed that the acid and salt combine to form a compound and the values of  $[\alpha]_D$  are calculated and plotted against the weight of ammonium molybdate added, the curve shows a steep rise to a maximum and then a rapid fall. A solution having the composition corresponding with this maximum, when evaporated, gave a crystalline compound having  $[\alpha] + 219^\circ$  for the yellow ray of mercury, and in addition a very sparingly soluble ammonium molybdate. W. G.

**The Specific Rotation of Lævulose.** WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1920, 42, 1696—1704).—From measurements of the rotation of levulose solutions at  $25^\circ$  the concentration varying from 2.6 to 20 grams per 100 c.c., the author deduces the formulæ  $[\alpha]_D^{25} = -(88.50 + 0.145p)^\circ$  or  $[\alpha]_D^{25} = -(88.50 + 0.150c - 0.00086c^2)^\circ$ , where  $p$  is the percentage by weight of the sugar in the solution and  $c$  the number of grams per 100 c.c. Over the temperature range  $15-37^\circ$  the variation of  $[\alpha]$ , with temperature is given by  $[\alpha]_D^{25} = [\alpha]_D^{25} + (0.566 + 0.0028c)(t - 25)^\circ$ . The author considers that Ost's results (A., 1891, 1000) are best expressed by  $[\alpha]_D^{25} = -(91.50 + 0.133p)^\circ$ .

For most purposes the values of  $[\alpha]_{D=486m}^{25}$  are given by  $1.1809[\alpha]_D^{25}$ , although the coefficient seems to vary very slightly with temperature and concentration. W. G.

**An Apparatus for using in Photochemical Reactions the Luminous Energy Emitted by an Incandescent Lamp.** V. VOLMAR and C. DUFRAISSE (*Bull. Soc. chim.*, 1920, [iv], 27, 680—681).—A simple arrangement is described by means of which the necessary metallic filament lamp can be introduced into the reaction liquid contained in a glass vessel surrounded by a polished metal jacket, the whole being immersed in a bath by which the temperature can be controlled. W. G.

**Experimental Decision of the Question of the Radioactivity of all Elements.** G. HOFFMANN (*Ann. Physik*, 1920, [iv], 62, 738—758).—A special very sensitive electroscope capable of photographic registration upon a chronograph and sensitive to 5000 ions per mm., or a deflection of 30 mm. per single  $\alpha$ -particle, has been used to investigate the "natural" radioactivity of common materials. From the range of the  $\alpha$ -particle it can be decided whether the radioactivity is due to known or new radio-elements. The range can be obtained by statistical methods from the observation of the ionisation produced by each  $\alpha$ -particle for a large



number. A discussion of the results obtained for the natural ionisation of a hollow sphere of brass proves that it is not wholly due to radium and its derivatives or to thorium, but in large part to new  $\alpha$ -rays of very short range from a very long-lived radio-element. The material emitted 0.108  $\alpha$ -particle per  $\text{cm}^2$  per hour, with a maximum ionisation of 100,000, corresponding with a range of about 1.8 cm. at *N.T.P.* The period of the element producing it (? copper) must be at least  $1.5 \times 10^6$  times that of uranium, and this agrees with the range found.

F. S.

**Reactions in Penetrating Radium Radiation and in Ultra-violet Radiation Filtered by Quartz Glass.** ANTON KAILAN (*Zeitsch. physikal. Chem.*, 1920, **95**, 215—246).—Mixtures of fumaric and maleic acids containing respectively 24, 40, 48, and 64% of maleic acid have been subjected, in 1/50*N*-solutions for 2 to 3000 hours at 6—14°, to the radiation of 80—110 mg. of radium metal through 1 mm. of glass. On the assumption that the decrease in the titre of the solution (5—7%) is due to the formation of acrylic acid, it is found that in all cases but one the maleic acid concentration has increased. This follows from conductivity measurements on the radiated solutions. When the above assumption is approximately true the position of the equilibrium point is much the same when the solution has been radiated with either ultra-violet rays or with radium rays, namely, 72% at 45—50°. Neither by 1632 hours' radiation with the rays from 80 mg. of radium metal, nor by 48 hours' radiation from a quartz mercury lamp, is the density, the refractive index, or the velocity of change into ammonium cyanate, of a normal solution of urea, changed to an extent outside the experimental error. Between 25° and 37° the reaction velocity is increased fourfold for a temperature increase of 10°, which agrees with the measurements of Fawsitt at 90—99° (*A.*, 1903, ii, 15). Similar treatment of aqueous solutions of formic acid changes neither the dissociation constant nor the amount of oxalic acid formation. Both types of radiation induce a decrease in the titre of the solutions, the rate of which decreases as the concentration increases. Only rays with a smaller wave-length than  $0.34 \mu$  are active. A similar treatment of aqueous solutions of benzoic acid produces reducing substances, formic acid and oxalic acid; the velocity of formation of these substances increases as the square of the concentration of the benzoic acid. In this case also only rays smaller than  $0.34 \mu$  are active. The time in which the same effects are brought about by radium rays and by ultra-violet light is in the case of formic acid 270:1 and benzoic acid 7:1.

J. F. S.

**Colouring and Thermoluminescence of Glass produced by Radium Emanation.** S. C. LIND (*J. physical Chem.*, 1920, **24**, 437—443).—A theoretical paper in which the colouring of glass and other materials by radium emanations is discussed. It is shown that all three types of ray have the same effect on the glass, and

that the colouring takes place when pure substances are exposed to the rays. The colour is discharged from both glass and quartz by heating at a temperature at which the former substance commences to soften. Violet glass is slowly decolorised by exposure to sunlight, whilst brown glass is changed to a bright yellow by sunlight or ultra-violet light. When a piece of violet glass is heated at temperatures below  $200^{\circ}$  in the dark it luminesces for a period which is longer the lower the temperature, and after it has ceased to luminesce a further exposure to the radiation is necessary before further luminescence is possible. In this process, however, the violet colour is not affected; the colour only disappears when the temperature is raised to about  $500^{\circ}$ , and there is no luminescence in the temperature interval  $200-500^{\circ}$ . The more recently the glass has been subjected to the radiation the lower is the temperature at which luminescence occurs; glass which has been recently exposed to radiation commences to luminesce well below the boiling point of water, whilst glass which has been kept for two to three years after exposure only luminesces at  $200^{\circ}$ .

J. F. S.

#### **Solubility of Radium Emanation in Organic Liquids;**

ALFRED SCHULZE (*Zeitsch. physikal. Chem.*, 1920, **95**, 257—279).—The solubility of radium emanation has been determined in toluene, ethyl ether, chloroform, acetone, carbon disulphide, ethyl acetate, ethyl alcohol, hexane, water, aniline, and benzene at various temperatures with the object of testing Dolezalek's theory of gas solubility (A., 1910, ii, 184). The results show that this theory represents the experimental facts in a qualitative manner for the solubility of radium emanation, both in normal and associated solvents. As to the quantitative aspect of the case it is impossible to draw any conclusions because the amount of radium emanation dissolved is small, and measurements are thereby rendered very inexact. Despite this, it is possible to obtain trustworthy data of the solubility from measurements of the vapour tension of the emanation if the correct molecular weight of the solvent is brought into the calculations. On the other hand, it is possible to deduce directly, from the course of the solubility curve, trustworthy values of the molecular weight of the solvent and so gain an insight into the molecular condition of liquids.

J. F. S.

#### **Geiger-Nuttall Equation.** GERHARD KIRSCH (*Physikal.*

*Zeitsch.*, 1920, **21**, 452—456).—Application is made of the hypothesis that the atomic nucleus consists exclusively of helium and hydrogen nuclei with electrons, and of the Geiger-Nuttall relation in the form given by Lindemann (A., 1915, ii, 720), to deduce regularities in the disintegration series of radium and thorium. From these regularities, applied to the actinium series, conclusions are formed as to the atomic weights of these elements. An attempt is also made to show that there are three radioactive disintegration series.

J. R. P.

**$\alpha$ -Ray Rules.** HANS TH. WOLFF (*Physikal. Zeitsch.*, 1920, 21, 393—396).—The rule  $\log R = x \log (K - s) + y$ , where  $\log R$  is the common logarithm of the range of the  $\alpha$ -ray in cm. at N.T.P.,  $x$  a positive, and  $y$  a negative constant,  $K$  a constant, and  $s$  the order of the change in the disintegration series in which the  $\alpha$ -particle is expelled, counting for the first  $s=0$ , the second  $s=1$ , and so on, represents the ranges of the  $\alpha$ -rays of all four series approximately, the uranium series being considered two, from uranium-*I* to radium, and from radium emanation to radium-*C'*, polonium, actinium-*X*, actinium-*C*, and thorium-*C'* being exceptions. The values of  $x$  and  $y$  change for each of the four series, and the value of  $K$  is one-fourth of the atomic weight for the thorium and first part of the uranium series, 58 and 60, and 54 and 55 for the second part of the uranium series and for actinium respectively.

Discussing this relation theoretically, by the aid of the quantum relation it is deduced that the  $\alpha$ -particle is travelling in an orbit of radius  $\rho$  in the nucleus, given by the relation  $\rho = (K - s)^{-x/2}$  const.

F. S.

**Electron Affinity of the Sulphur Atom.** M. BORN and ELIZABETH BORMANN (*Zeitsch. Physik*, 1920, i, 250—255).—X-Ray measurements of the crystal lattice of zinc sulphide and application of the lattice theory lead to the value of 50 for the electron affinity of the sulphur atom. This value corresponds with an ionisation potential of 2.16 volts.

CHEMICAL ABSTRACTS.

**Conductivity and Frequency.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1920, 42, 1648—1655).—It is suggested that the conductivity of solutions of electrolytes is smaller at zero frequency than at any frequency in a certain range immediately above zero. Measurements of *N*-potassium chloride and sulphuric acid of maximum conductivity are described, and it is shown that the difference between direct current conductivities and those at 1000 cycles does not exceed 0.02—0.03%, but the difference lies in the direction expected. The conductivity of *N* potassium chloride at 25° given by Kohlrausch is confirmed within 0.1%.

J. F. S.

**The Thermoelectric Power of Pure Metals.** H. PELABOV (*Ann. Physique*, 1920, [ix], 13, 169—187).—From a study of the variation of the thermoelectric power with temperature, at temperatures above the melting point of one metal of the couples, it is shown that the thermoelectric power of pure metals varies continuously with the temperature, there being no discontinuity at the melting point. For the metals in the liquid state the thermoelectric power is a linear function of the temperature, at least for lead, tin, and bismuth. For antimony the results are not so regular.

W. G.

**Theory of Electrocapillarity. I. and II.** ALEXANDER FRUMKIN (*Phil. Mag.*, 1920, [vi], 40, 363—375, 375—385).—I. Gouy's theory

(A., 1917, ii, 291) that the superficial electric charge is zero at the maximum of the electrocapillary curve, but that there may be a potential difference between the mercury and the solution, due to adsorbed ions, is confirmed. The ordinary equation of the electrocapillary curve  $\partial\gamma/\partial\psi = \epsilon$  is replaced by  $\partial\gamma/\partial\psi = \epsilon + \Gamma_{H_2}F$ , where  $\gamma$ =surface tension,  $\epsilon$ =electric charge on unit surface of the mercury,  $\psi$ =potential difference between a decinormal calomel electrode and the mercury in the solution,  $\Gamma_{H_2}$ =adsorption excess of mercury in gm. equiv. per sq. cm. of dividing surface,  $F$ =96,540 coulombs. The results are incompatible with Nernst's theory, based on electrolytic solution pressure, since the potential difference between solution and mercury is not necessarily connected with exchange of ions of mercury, but may be caused solely by adsorbed layers of anions and cations.

II. A modification of Gibbs's adsorption equation is deduced, in which separate account is taken of the adsorption of the anion and the cation, and is used to calculate the horizontal distance between the ascending and descending branches of electrocapillary curves at different concentrations (Gouy, *loc. cit.*). The results are in fair agreement with the observed values, but the calculation of the maximum is less satisfactory. J. R. P.

**Activities of Ions in Aqueous Solutions of some Strong Electrolytes.** FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1920, 42, 1556—1564. Compare Noyes and MacInnes, this vol., ii, 345).—The *E.M.F.* of cells of the type  $Hg, HgCl | MCl(c_1) || MCl(c_2) | HgCl, Hg$ , in which *M* is sodium, potassium, or hydrogen, and in which the concentrations varied over wide limits, have been measured at 25°. In addition, the two cells  $Hg, HgCl | 0.1N KCl | 0.1N NaCl | HgCl, Hg$  and  $Hg, HgCl | 0.1N KCl | 0.1N HCl | HgCl, Hg$  have also been carefully measured, and from the results the activities of the ions have been calculated. The results show, as in the work of Beattie and MacInnes (this vol., ii, 467), that the conductivity-viscosity ratio does not afford a trustworthy measure of the activity of the ions of strong electrolytes. Furthermore, the marked increase in the activity-coefficient of hydrochloric acid, which occurs beyond 0.5*N*, proves conclusively that this quantity cannot be proportional to the degree of ionisation. J. F. S.

**Electromotive Behaviour of Aluminium. I.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 22, 876—881).—A theoretical paper in which an explanation of the valve action of aluminium is put forward. The ennobling of the aluminium potential on anodic polarisation occurs as follows. During the withdrawal of electrons from the metal, represented by  $3\theta_s$ , aluminium ions pass into solution,  $Al^{+++} \rightarrow Al^{+}$ , and because this heterogeneous equilibrium is established instantaneously the reaction  $Al_s \rightarrow Al_s^{+++} + 3\theta_s$  proceeds with a very small velocity, so that the metal becomes poorer in ions and electrons. In consequence of this the potential of the metal becomes more positive, as is seen from the

equation  $E = 0.058/\nu \cdot \log I_w/M_i - 2.8$ , because in this case  $I_w$  becomes smaller. Since the metal is inert the discharge potential of oxygen will soon be reached and oxygen will be liberated, which in certain circumstances may lead to the formation of an adherent coating of oxide on the metal. This coating gives rise to a certain resistance which may rise to a considerable value with increasing thickness. The assumption, however, that the resistance of such a coating should be different for different directions of the current is not justifiable, so that the sudden decrease of resistance on reversal of the current must be due to another cause. The small quantity of oxygen absorbed by the metal is a negative catalyst towards the setting up of the internal metal equilibrium. Hence the metal surface, being very poor in ions and electrons, passes into a metalloid condition, that is, it possesses small conductivity. Hence on anodic disturbance the aluminium surface becomes a metal layer of great resistance, and this coating is in turn surrounded by another of alumina. On reversal of the current the hydrogen liberated removes the absorbed oxygen, and the aluminium surface is transformed with great velocity into a condition of internal equilibrium, that is, the coating of great resistance is changed into one of negligible resistance. Hence the resistance remaining when aluminium is changed from anode to cathode is chiefly the resistance of the alumina.

J. F. S.

**Ignition of Gases at Reduced Pressures by Impulsive Electric Sparks.** W. M. THORNTON (*Phil. Mag.*, 1920, vi, 40, 345—356).—Ignition by impulsive sparks is, on the whole, more difficult at low pressures, in this differing from ignition by hot wires. In hydrogen and methane the increase of difficulty takes place by well-marked steps or stages. In ethane or propane this does not occur, but there is an oscillation of the curve, found also in hydrogen and carbon monoxide. This appears to be associated with the temperature of the parking point during the passage of the spark. It has been shown previously (*A.*, 1911, ii, 524, 834; 1915, ii, 751) that at pressures well above atmospheric sudden changes of inflammability occur when ignition is by impulsive sparks or condenser discharge. It is now found that there are such steps at reduced pressures, and that there is a close agreement between the partial pressures corresponding with the points at which oxygen has ratios to the mass of the combustible gas expressed by successive natural numbers, and the pressures at which sudden changes of inflammability occur.

J. R. P.

**Dye Cells.** E. STAEGELIN (*Zeitsch. physikal. Chem.*, 1920, 94, 542—591).—The change in *E.M.F.* produced in cells containing various fluorescent dyes on illumination with a 300 candle-power half-watt lamp has been measured against a *N-calomel* electrode. Rhodamine-B, rhodamine-3B, sodium eosin, quinino sulphate, tetrachlorofluorescein, the phosphine dye, the sodium salts of  $\beta$ -naphthylamine-6:8- and 5:7-disulphonic acids,

and resorufin, were all measured both alone in solution and in the presence of oxidising and reducing agents, such as acetaldehyde, formaldehyde, oxalic acid, ferrous sulphate, iodine, vanadium tetroxide in sulphuric acid, ferric sulphate, hydrogen, oxygen, quinol, and other substances, such as potassium chloride, iodide, and sodium carbonate. It is shown that the Becquerel effect takes place in both directions, and its dimensions and direction depend on the presence of reducing and oxidising agents. The behaviour of all the cells examined can be explained by the assumption of a hidden oxygen-hydrogen photolysis.

J. F. S.

**Metastability of the International Weston Element and its Unsuitability as an [Electrical] Tension Normal.** ERNST

COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, 95, 285—304).—The international Weston element with a 12.5% cadmium amalgam, which was recommended by the international conference on electrical standards and units (Washington, 1908), does not fulfil the demands which are required from a standard of electromotive force. This is because the results of Cohen (A., 1900, ii, 702), Bijl (A., 1903, ii, 6), and F. E. Smith (*Collected Researches Nat. Phys. Lab.*, 1910, 6, 137) on the composition of the element have not been sufficiently taken into account. This element at temperatures below 12° is a metastable system, which may spontaneously become stable with a noticeable change in the *E.M.F.* amounting to about 6 millivolts at 0°, and for this reason is unsuitable as a standard. The temperature formula recommended by the conference for use between 0° and 10° with this element refers to elements which are metastable up to 12° and stable above this temperature. The Weston element is to be replaced by an element containing 8% admium amalgam as recommended by Cohen and Kruyt (A., 1910, i, 178, 259), which is stable from a few degrees below zero to 40°. The temperature formula mentioned above is strictly applicable to elements containing 8% cadmium amalgam from 0° to 40°, and may be applied to all such elements which are stable over this range of temperature. The Weston elements supplied by the Weston Company containing 12—13% cadmium amalgam are also unstable below 12°, and are also unsuitable as normals of electromotive force.

J. F. S.

**Moving Striations in Neon and Helium.** F. W. ASTON

and T. KIRCH (Proc. Roy. Soc., 1920, [A], 98, 50—56).—When the flash of an ordinary spectrum tube containing neon or helium is analysed by a rotating mirror it is found to consist of an extremely short flash followed by a flame or arc, and that the latter consists of bright striations travelling from anode to cathode. The velocity of these striations is found to be about 50,000 cm./sec. in neon and 100,000 cm./sec. in helium. These values are a limiting case, and the velocity varies with varying conditions, such as pressure, diameter of tube, and temperature. Neither air nor hydrogen

showed moving striations in capillary tubes, but in a tube 1.6 mm. wide both developed stationary striations at 1 mm. to 2 mm. pressure. J. F. S.

**Variation of Magnetic Susceptibility during Allotropic Transformations and Melting of some Substances.** TORAJIRŌ ISHIWARA (*Sci. Rep. Tohoku Imp. Univ.*, 1920, 9, 233—241).—The magnetic susceptibility of five weakly magnetisable substances was examined over considerable ranges of temperature in a modified torsion balance apparatus which could be exhausted or filled with inactive gas. Water was used as the standardising substance of the apparatus, its specific susceptibility being accurately known. Silver bromide is diamagnetic. On cooling, its susceptibility is fairly constant down to 200°, below which there is a slight decrease but no discontinuity in passing through the melting point. Silver chloride is also diamagnetic, the susceptibility increasing with rising temperature, with no discontinuity during fusion. The diamagnetic susceptibility of sulphur shows no discontinuity at the transformation from rhombic into monoclinic crystals, and the curves give no definite indication of fusion, but the transformation in the liquid phase at 160—170° is accompanied by a decrease of about 2% in diamagnetism, after which the susceptibility is again constant. There are indications of a reversible magnetic change at about 80° which may be due to the presence of an amorphous sulphur. The diamagnetic susceptibility of zinc shows a sudden decrease of about 4% at the melting point with a linear decrease above and below this point. Aluminium is paramagnetic, and its susceptibility is constant over a range of 100° below its melting point. During fusion it increases by about 2% and then remains constant.

T. H. B.

**Molecular Theory of the Paramagnetism of Solid Salts.** OTTO STERN (*Zeitsch. Physik.*, 1920, i, 147—153; from *Chem. Zentr.*, 1920, iii, 297). Curie's law,  $\chi T = \text{const.}$  (where  $\chi$  is the susceptibility and  $T$  the absolute temperature), has been applied by Weiss to solid substances on the basis of Langevin's theory and on the assumption that here also the molecules, as carriers of the elementary magnets, are able to rotate freely. Since, however, doubts have been cast on this assumption, Weiss endeavoured to show later that it is not really essential if the condition is fulfilled that the molecules are attached to stable equilibrium positions or, in consequence of temperature changes, oscillate round these positions, provided only that the orientation of these equilibrium positions does not occur in any preferential direction (amorphous substances and crystalline powders). The detection of an error in Weiss' calculations has led the author to recalculate the entire subject. He is led to the diametrically opposite conclusion that the susceptibility of such a substance is independent of the temperature to a first approximation, and only as a second approximation decreases somewhat but only very slightly with increasing tempera-

ture—a result which could be predicted without calculation. Curie's law cannot therefore be valid for molecules oscillating round an equilibrium position, but only for such as are able to rotate freely. Since the molecules in a crystal certainly do not conform to this condition and Curie's law is known to be valid, the author is led to the conclusion that the molecules cannot be regarded as the carriers of the magnetic moment, and that this function is probably performed by the ions. H. W.

**Volume Change Produced on Diluting Concentrated Solutions or Mixing Two Liquids.** [FRL.] IRENE D. GÖRZ (*Zeitsch. physikal. Chem.*, 1920, 94, 181—209).—The thermal expansion of ethylene dichloride, benzene and ethyl ether under a pressure of 420 and 350 atms. respectively has been determined over the range 0—40°; the volume change is represented by the following equations: ethylene dichloride,  $v = 0.78025(1 + 0.0011109t + 0.000001696t^2)$ ; ethyl ether,  $v = 1.35786(1 + 0.0015006t + 0.00000437t^2)$ ; benzene,  $v = 1.11250(1 + 0.0011715t + 0.000000155t^2)$ . The thermal expansion of mixtures of ethyl ether-ethylene dichloride and ethyl ether-benzene of various concentrations has been determined and found to be the same as that of ethyl ether under definite external pressure. These pressures were proportional to the concentration of the ethylene dichloride up to 49.875% and to that of the benzene up to 100%. Making use of Tammann's law of concentrated solutions, the contraction on mixing a concentrated solution of ethylene dichloride in ethyl ether with ethyl ether has been calculated and the values found to be very near the experimentally determined value. The contraction on mixing ethyl ether with benzene has been calculated on the assumption that two liquids only differ from one another and from their mixture in respect of their internal pressure, and the volume change depends only on the total pressure. The calculated values are very nearly those determined experimentally, except in a few cases.

J. F. S.

**Graphic Representation of the Characteristic Equation.** R. MOLLIER (*Physikal. Zeitsch.*, 1920, 21, 457—463).—The magnitude  $y = pv^2/T$  is plotted as ordinate against the density or the reciprocal of the absolute temperature as abscissa. The resulting diagrams for different characteristic equations are discussed.

J. R. P.

**Theory of the Solid State of Aggregation.** A. VAN DER WERTH (*Zeitsch. physikal. Chem.*, 1920, 95, 129—138).—A theoretical paper in which a number of properties of solids are treated mathematically. It is shown that the specific heat and the mechanical solidity bear a simple relationship to one another. Both quantities depend on the molecular attraction, and furnish a measure of the resistance with which a substance opposes any force which tends to disrupt it. This resistance is termed the "work of expan-



sion," and may be calculated from the modulus of elasticity and also from the specific heat and the thermal expansion. The following relative values have been calculated for the lengthening by 1/100 mm. of the following substances, from the specific heat values: Al, 8.05; Pb, 5.2; Cd, 8.07; Fe, 31.25; Au, 18.08; Cu, 20.37; Na, 0.168; Ni, 29.7; Pd, 24.45; Pt, 32.7; Ag, 12.7; Bi, 9.41; Zn, 9.67; and Sn, 7.1. The values calculated from the modulus of elasticity in many cases differ very much from the above values. The method adopted in the above calculations permits of qualitative conclusions being drawn in connexion with the mechanical properties of solid substances from simple thermal data.

J. F. S.

**An Electrical Adiabatic Calorimeter and its Use in the Determination of the Specific Heat of Solutions of Cadmium Sulphate.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **95**, 305—327).—The construction of an adiabatic calorimeter is described, which in its chief points follows closely the adiabatic calorimeter of Richards (A., 1908, ii, 806). The main point of difference lies in the heating of the liquid in the protecting jacket. Richards changed the temperature of the jacket by neutralising sodium hydroxide solution at a measured rate, whilst in the present case the change in temperature is effected by the passage of a known amount of electrical energy into the water in the surrounding jacket. An accuracy of 0.5 per 1000 is claimed for the results obtained with this instrument. The specific heat of solutions of cadmium sulphate from 1.89% to 44.63% (by weight) has been determined and values obtained which steadily fall from 0.9763 with the most dilute solution to 0.5725 with the most concentrated. The results are compared with the values obtained by Berthelot-Thomsen and found to differ by quantities varying from 1/7000 to 36/6000.

J. F. S.

**Indirect Method of Determining the Specific Heat of Dilute Solutions with Preliminary Data Concerning Hydrochloric Acid.** THEODORE W. RICHARDS and ALLAN W. ROWE (*J. Amer. Chem. Soc.*, 1920, **42**, 1621—1635).—The specific heat of a dilute solution can be determined indirectly from the difference in the heat developed on diluting a known concentrated solution to a solution of the desired strength at two temperatures. The method is based on Kirchhoff's law,  $K_v - K'_v = (U' - U)/\Delta\theta$ , in which  $K_v$  and  $K'_v$  are the molecular heat capacities of the two substances,  $U$  and  $U'$  the respective total energy changes, that is, the heats of dilution at  $\theta$  and  $(\theta + \Delta\theta)$ . This method has been carried out with the utmost care for solutions of hydrochloric acid. The following molecular heats of dilution have been obtained for 20°:  $\text{HCl.10H}_2\text{O} + 15\text{H}_2\text{O}$ , 714 cal.;  $\text{HCl.10H}_2\text{O} + 40\text{H}_2\text{O}$ , 949;  $\text{HCl.10H}_2\text{O} + 90\text{H}_2\text{O}$ , 1082;  $\text{HCl.20H}_2\text{O} + 80\text{H}_2\text{O}$ , 480;  $\text{HCl.10H}_2\text{O} + 190\text{H}_2\text{O}$ , 1161;  $\text{HCl.20H}_2\text{O} + 180\text{H}_2\text{O}$ , 549;  $\text{HCl.10H}_2\text{O} + 390\text{H}_2\text{O}$ , 1219;  $\text{HCl.10H}_2\text{O} + 790\text{H}_2\text{O}$ , 1247. The following specific heats, for which

an accuracy of about 0.05% is claimed, have been obtained:  $\text{HCl}, 10\text{H}_2\text{O}$ , 0.752;  $\text{HCl}, 20\text{H}_2\text{O}$ , 0.849;  $\text{HCl}, 25\text{H}_2\text{O}$ , 0.8776;  $\text{HCl}, 50\text{H}_2\text{O}$ , 0.9320;  $\text{HCl}, 100\text{H}_2\text{O}$ , 0.9634;  $\text{HCl}, 200\text{H}_2\text{O}$ , 0.9812; and  $\text{HCl}, 400\text{H}_2\text{O}$ , 0.9905. This method of determining specific heats is to be recommended because it is easier to measure two heats of dilution than one direct specific heat.

J. F. S.

### Variation of the Specific Heat of a Gas with Temperature.

GÉORGE W. TODD (*Phil. Mag.*, 1920, [vi], 40, 357—362).—It is shown that continuous change of specific heat with temperature is not inconsistent with the theory of equipartition, and that the data for hydrogen are explained by the theory of equipartition as well as by the quantum hypothesis. It is assumed that gas molecules have three degrees of freedom so long as their velocities are below a critical value; above this value collisions result in the acquisition of further degrees of freedom.

J. R. P.

### Specific Heat of Saturated Vapours at Low Temperatures.

E. ARFÈS (*Compt. rend.*, 1920, 171, 456—458).—A criticism of Bruhat's work (this vol., ii, 528), in which the author reaffirms his own views on the subject (*A.*, 1917, ii, 192).

W. G.

### Third Law of Thermodynamics and the Entropy of Solutions and of Liquids.

GILBERT N. LEWIS and G. E. GIBSON (*J. Amer. Chem. Soc.*, 1920, 42, 1529—1533).—A theoretical paper in which the Nerst third law of thermodynamics and the entropy of liquids and solutions are considered. The third law of thermodynamics is restated as follows: "If the entropy of each element in some crystalline form is taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero and the entropy of any other substance is greater than zero." It is, however, likely that the difference between the entropy of a pure substance in the crystalline state and in any amorphous state may, in many cases, prove to be very small.

J. F. S.

### Entropy Changes at Low Temperatures. I. Formic Acid and Carbamide. A Test of the Third Law of Thermodynamics.

G. E. GIBSON, W. M. LATIMER, and G. S. PARKS (*J. Amer. Chem. Soc.*, 1920, 42, 1533—1542).—The specific heat of formic acid and of carbamide has been determined at a large number of temperatures from 71.0° K to 300.3° K. For formic acid the following values have been obtained: 71.0° K,  $C_p$  per gram = 0.157; 90.3° K,  $C_p$  = 0.182; 250.5° K,  $C_p$  = 0.344; and 291.5° K, 0.510; for carbamide the results include: 86.4° K,  $C_p$  = 0.239; 107.5° K,  $C_p$  = 0.259; 244.2° K,  $C_p$  = 0.382; and 300.3° K,  $C_p$  = 0.460. From these values the free energy and entropy have been calculated, and the following values, which are in keeping with the third law of thermodynamics (see preceding abstract), are obtained: Formic acid,  $S_{298.15^\circ}$  = 4.72 per atom, and  $S_{298.15^\circ}$  = 4.86 per atom or 24.30 per mol.; the entropy of fusion is 8.60.

$S_{298}^{\circ}(\text{liquid}) = 34.2$ . The free energy of formation from the elements is  $-85370$  cal., and from carbon monoxide and water  $3415$  cal., both at  $298^{\circ} K$ . Carbamide,  $S_{298}^{\circ} = 41.0 \pm 2.0$ , and the free energy of formation from the elements is  $\Delta F_{298}^{\circ} = -48,992$  cal. J. F. S.

**Entropy Changes at Low Temperatures. II. Ethyl and Propyl Alcohols and their Equimolecular Mixture.** G. E. GIBSON, G. S. PARKS, and W. M. LATIMER (*J. Amer. Chem. Soc.*, 1920, **42**, 1542—1550. Compare preceding abstract).—The specific heat of ethyl alcohol, propyl alcohol, and an equimolecular mixture of the two has been determined for the liquids, crystalline solids, and the glasses at temperatures from  $78.5^{\circ} K$  to  $274.6^{\circ} K$ . The heat of fusion of ethyl alcohol at the melting point  $156.2^{\circ} K$  is found to be  $24.0$  cal. per gram or  $123$  cal. per gram-atom. The molecular heat capacities are: ethyl alcohol,  $268.7^{\circ} K$ ,  $24.39$ ;  $198.3^{\circ} K$ ,  $21.10$ ;  $90.0^{\circ} K$ ,  $12.80$ ; and  $86.0^{\circ} K$ ,  $12.15$ ; propyl alcohol,  $268.7^{\circ} K$ ,  $30.96$ ;  $198.3^{\circ} K$ ,  $26.67$ ;  $90.0^{\circ} K$ ,  $15.17$ ; and  $86.0^{\circ} K$ ,  $14.47$ , whilst the values for the equimolecular mixture at the same temperatures are  $27.72$ ,  $23.83$ ,  $13.90$ , and  $13.21$  respectively. From the data it appears probable that the entropy of the equimolecular mixture is not zero at the absolute zero. Assuming the validity of the third law of thermodynamics to the process ethyl alcohol (supercooled)  $\rightarrow$  ethyl alcohol (crystalline)  $\Delta S_{156.2}$  has been calculated by two methods. The difference (per gram-atom) between the results obtained is  $0.12$  cal. per degree or  $20$  cal. at  $156.2^{\circ} K$ . By means of the third law of thermodynamics the free energy of ethyl alcohol has been calculated to  $F_{298}^{\circ} = -43,000$  cal. J. F. S.

**Space-filling and Ionic Mobility.** RICHARD LORENZ (*Zeitsch. Elektrochem.*, 1920, **26**, 383—384).—The author refers to the work of H. Kauffmann (this vol., ii, 16) as of importance in the extrapolation of electric conductivities to the limiting value, but differs from him in considering the boiling points as corresponding states for liquids. J. R. P.

**Some Little-noted Sources of Error in Boiling-point Determinations under Reduced Pressure.** C. VON RECHENBERG and E. BRAUER (*Zeitsch. physikal. Chem.*, 1920, **95**, 184—214).—A large number of experiments on the determination of boiling points under reduced pressure are described. It is shown that the temperature of the vapour in the boiling tube decreases from the bottom upwards, in individual cases as much as  $20^{\circ}$ . The electrically determined temperature measurements of Hansen (*A.*, 1910, ii, 827) show that there is a more rapid fall of temperature between the surface of the boiling liquid and a height  $1$ – $2$  cm. above it than elsewhere, which may be explained by the presence of fine drops of superheated liquid carried upward by the vapour. The temperature gradient in the upper half of the boiling tube is regular, and occasionally greater than in the lower half. The temperature fall therefore increases from the bottom upward, and this is true in all cases.

and with all variations of heating and temperature of the mantle. With increase in the heating, that is, with increase in the amount of vapour evolved, the temperature increases at all points in the boiling tube, but in general the temperature gradients and temperature differences do not change to any marked extent. The temperature of the surrounding mantle influences the temperature of the vapour to a marked extent. The following conditions are recommended for the determination of boiling points by the dynamic method. The boiling flask may be of glass or metal; in the latter case a flattened bottom is preferable, whilst in the case of glass a second neck carrying a capillary tube is advantageous. The neck of the flask should be surrounded with a vapour mantle; the boiling tube must be at least 20 mm. wide, the neck and condenser tubes 15 mm. wide. The thermometer bulb must be placed at least 50 mm. above the level of the boiling liquid and the whole of the mercury thread should be in the vapour. Pressure measurements should be made on the boiling tube. The manometer should have a limb 15 mm. wide and must be perfectly vertical, and pressures of less than 5 mm. should not be measured in this way. The velocity of distillation must never be greater than one drop per second, and no temperature or pressure readings should be made until at least 10 c.c. have distilled over.

J. F. S.

**The Boiling Points, Critical Temperatures and Pressures in Homologous Series.** MACRICE PRUD'HOMME (*J. Chim. physique*, 1920, 18, 94—102).—In a homologous series the value of  $T_b/T_c$  increases from one member to the next higher in the series,  $T_b$  being the absolute boiling point and  $T_c$  the absolute critical temperature.  $(T_c - T_b)$  increases or decreases similarly according to the particular series, and  $T_b/T_c$  divided or multiplied by  $(T_c - T_b)$  is a constant for each series.

The difference in the critical temperatures of two adjacent members in the series of paraffin hydrocarbons is given by  $\Delta = 210/T_c^{0.01857\sqrt{T_c}}$ .

For isomeric esters,  $(T_c - T_1)/(T_c - T_2)$  is a constant, where  $T_1$  and  $T_2$  are the absolute boiling points at two different pressures. Further,  $(T_c - T_1)$  is an exponential function of the critical pressure.

The introduction of any one of the halogen elements into a hydrocarbon gives for  $T_b/T_c$  and  $T_c/(T_c - T_b)$  constant values independent of the nature of the halogen.

W. G.

**Ulrich Dühring's Law of Boiling Points at Similar Pressures. The Zero Point of Vaporisation.** C. VON RECHENBERG (*Zeitsch. physikal. Chem.*, 1920, 95, 154—183).—A theoretical paper in which Dühring's rule is examined by means of a large amount of previously published vapour pressure data. It is shown that this rule may be restated as follows. The saturation temperatures, for equal pressures of pure uniform chemical substances having similar vapour-pressure curves, change in the same way if the compounds during vaporisation do not change their

constitution, that is, neither dissociate nor associate, and when the vapour is entirely unimolecular. The author postulates a minimum temperature at which a substance ceases to exert a vapour pressure; this is the temperature at which vapour ceases to be capable of existence, and is termed the zero of vaporisation; it differs for every substance, and if it is found experimentally for a single substance can be calculated for all others by Dühring's rule. The vaporisation zero of hydrogen is the same as the absolute zero, as follows from the vapour-pressure determinations of Travers, Senter, and Jaquero (A., 1903, ii, 9). Using this value, those of about fifty other substances have been calculated. The values of the more common substances are: oxygen,  $-243.91^{\circ}$ ; carbon dioxide,  $-171.49^{\circ}$ ; ammonia,  $-161.83^{\circ}$ ; chlorine,  $-182.29^{\circ}$ ; ethyl ether,  $-146.73^{\circ}$ ; ethyl alcohol,  $-91.96^{\circ}$ ; benzene,  $-129.71^{\circ}$ ; water,  $-87.84^{\circ}$ ; benzoic acid,  $+1.73^{\circ}$ ; glycerol,  $+27.85^{\circ}$ ; and sulphur,  $6.57^{\circ}$ . J. F. S.

**Vapour Pressure Equation.** CYRIL H. MEYERS (*Phil. Mag.* 1920, [vi], 40, 362-363).—The equation of Todd and Owen (A., 1919, ii, 495) is criticised adversely. J. R. P.

**Approximation Formulæ for Univariant Systems.** J. A. VAN LIEMPT (*Zeitsch. anorg. Chem.*, 1920, 111, 280-288).—A theoretical paper in which the author deduces formulæ by which the vapour pressure and sublimation pressure in univariant systems may be approximated from known data. The formulæ are based on the Clapeyron formula,  $dp/dT = Q_v/(v_g - v_l)T$ , and have the form  $\pi = -0.2184k_1T_k\tau + 0.2184k_1$ , in which  $k_1$  is the Trouton constant (21),  $T_k$  the boiling point, and  $\tau = 1/T$ , the temperature under discussion; supplying the value of the constants, the formula becomes  $\pi = -4.59T_k\tau + 4.59$ . This formula holds in the region of the critical point if it is written in the form  $\log p_{cr} = -4.59T_k/T_{cr} + 4.59$ . The sublimation pressure is given by  $\pi = -(2.95T_k + 4.59T_k)\tau + 7.53$ . J. F. S.

**Liquefaction of Air and the Characteristic Equation.** K. SCHREBER (*Physikal. Zeitsch.*, 1920, 21, 430-433).—A discussion of the Joule-Kelvin effect leads to the characteristic equation  $v^3 - (RT/p - a/T + c)v^2 - bR^2T = 0$ , instead of van der Waals's equation  $v^3 - (RT/p + b)v^2 - av^2/p + ab/p = 0$ . J. R. P.

**Heat of Reaction.** WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1920, 26, 385-391).—The energy content of a body consists of heat and potential energy, which are interconvertible. Nernst's theorem is deduced from this assumption. Kirchhoff's equation for the dependence of heat of reaction on temperature, and Nernst's use of the equation, are said to be incorrect. The author believes that affinity is independent of temperature. J. R. P.

**Heats of Combustion of Benzene, Toluene, Aliphatic Alcohols, cycloHexanol, and other Carbon Compounds.**

THEODORE W. RICHARDS and HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1920, **42**, 1599—1617).—The heat of combustion of a number of carbon compounds has been most carefully determined, and the following values obtained in 18° calories per gram: sucrose, 3943; benzoic acid, 6320; naphthalene, 9614; benzene, 10,014; toluene, 10,155; *tert*-butylbenzene, 10,434; cyclohexanol, 8882; diisooamyl, 11,339; methyl alcohol, 5326; ethyl alcohol, 7101; propyl alcohol, 8033; *n*-butyl alcohol, 8615; and isobutyl alcohol, 8599. The heat effect for the addition of CH<sub>2</sub> in alcohols, and in the side-chains of aromatic hydrocarbons, is 648 kilojoules or 153·5 Cal., whilst that for the addition of CH<sub>2</sub> in the benzene ring is 638 kilojoules.

J. F. S.

**Calculation of Theoretical Heats of Solution.**

H. VON STEINWEHR (*Zeitsch. physikal. Chem.*, 1920, **94**, 6—24).—A theoretical paper in which the calculation of the theoretical or fictitious heat of solution is considered. It is shown that the two most important methods for calculating this quantity, as put forward by Cohen and Bruins (*A.*, 1918, ii, 297), are only possible in the case of anhydrous salts. The method applicable to hydrates, which can also be applied to anhydrous salts, was deduced by W. Jaeger (*Ber. Deut. physikal. Ges.*, 1901, **3**, 48), and has now been developed without the objections which were raised to Jaeger's method, and it has been used to calculate the fictitious heat of solution of NaSO<sub>4</sub>·8/3H<sub>2</sub>O at 4° and the value -182·85 cal. obtained. The formula for calculating the temperature-coefficient of the fictitious heat of solution given by Cohen and Bruins (*loc. cit.*) is shown to be incorrect, and corrected formulae have been deduced for the cases applying to hydrates and anhydrous salts. The probable course of the fictitious heat of solution of CdSO<sub>4</sub>·8/3H<sub>2</sub>O, with temperature changes, has been calculated from the values calculated for -7·3°, 1°, and 18°. It is also shown that by making use of a modification of Kirchhoff's formula for the heat of solution, the fictitious heat of solution and the difference between the total energy of elements, may be calculated both for the conditions with and without solid phase if the dependence of the tension of aqueous vapour of the solution on the dilution of the solution and the temperature-coefficient of the solubility of the salt are known. These formulae hold for both anhydrous salts and hydrates.

J. F. S.

**Theory of Binary Mixtures. VI. Compressibility of Binary Mixtures.** F. DOLEZALEK and F. SPEIDEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 72—110).—The theory of the compressibility of binary mixtures is developed in connexion with the author's theory of binary solutions (this vol., ii, 32). The compressibility of the binary mixtures, benzene-ethylene dichloride, ethyl ether-chloroform, and benzene-carbon tetrachloride has been determined at 24·6° for all possible concentrations up to a pressure

of 600 kilo./sq. cm. The compressibility curve for mixtures of benzene and ethylene dichloride is a straight line at all pressures, which indicates, in keeping with previous vapour-pressure measurements (*loc. cit.*), that both substances are unimolecular and that the compressibility is additive at all concentrations. The compressibility curve for mixtures of ethyl ether and chloroform at lower pressures is strongly convex to the abscissa axis; consequently there is a strong deviation from simple additivity in the compressibility of these substances. If the amount of complex formation between these substances, previously found from vapour-pressure measurements, is taken into account, the curve becomes a straight line and exact additivity is obtained over the whole range of concentrations. With increasing pressure, in accordance with the theory, the curvature becomes less, and eventually it becomes concave to the abscissa axis. Mixtures of benzene and carbon tetrachloride exhibit at lower pressures a strongly concave compressibility curve, which is in keeping with the previous vapour-pressure measurements. If the formation of double molecules by the benzene is taken account of the compressibility for all concentrations becomes additive, and a straight line curve is obtained. With increasing pressure the curve becomes convex, as is demanded by the theory. J. F. S.

**Application of the Law of Limiting Densities to Easily Liquefiable Gases and the Atomic Weight of Sulphur.** EUGÈNE WOURTZEL (*J. Chim. physique*, 1920, **18**, 142—150).—In the light of Guye's recent work (A., 1919, ii, 318), the author has revised certain of his previous calculations (A., 1913, ii, 771), and in particular calculations of the results obtained by Jaquero and Scheuer on the compressibility of sulphur dioxide. From these calculations he deduces an atomic weight of sulphur,  $32.059 \pm 0.006$ .

W. G.

**The Viscosimeter as a means of Determining Density.** J. HOLKER (*J. Path. Bact.*, 1920, **23**, 185—187).—By combining the formulae of Ostwald-Poiseuille and of Scarpa (A., 1911, ii, 17), in which the density of the liquid does, and does not, occur respectively, it is possible to find the density by the viscosimeter. The results are in satisfactory agreement, and 2 c.c. or less of liquid are sufficient. J. R. P.

**Determination of Density by means of the Pyknometer.** WALTER BLOCK (*Zeitsch. angew. Chem.*, 1920, **33**, 198—200).—A discussion on the best way of using the pyknometer, attention being directed to sources of error in weighing, influence of atmospheric pressure, etc. W. P. S.

**Internal Friction of Binary Mixtures of Liquids.** JULIUS MEYER and BRUNO MYLIUS (*Zeitsch. physikal. Chem.*, 1920, **95**, 349—377).—The density and specific volume of benzene and fluoro-, chloro-, bromo-, and iodo-benzenes have been determined at tempera-

tures from 0° to the boiling point, and from calculations made from the Eötvös rule and the Trouton-Nernst formula it is shown that these substances are probably normal in the liquid condition. The density and specific volume of the binary mixtures of benzene and its halogen derivatives have been determined for various mixtures at temperatures between 0° and 80°. A comparison of the experimental specific volumes with those calculated by the mixture law from the individual specific volumes shows differences which lie within the experimental error, which indicate that the specific volume in these cases is an additive property. The viscosity-coefficient and fluidity of benzene and its monohalogen derivatives have been determined at temperatures between 0° and the boiling point. Below 95° fluorobenzene has a greater fluidity than benzene, despite its larger molecular weight. Above 95° the fluidity follows the expected order, that is, it is inversely proportional to the molecular weight. In all cases the  $v\phi$  curves are straight lines, and are in keeping with the Batschinski equation between  $v$  and  $\phi$  (A., 1913, ii, 928). The constants  $a$  and  $b$  of the Batschinski equation have been calculated for all five substances, and the observed and calculated values of  $\phi$  found to be extremely good. The fluidity of the binary mixtures mentioned above has been measured at temperatures 0–80°, and in these cases also the  $v\phi$  curves are straight lines. In general, the fluidity and internal friction cannot be calculated from any of the mixture formulae hitherto applied. The formula  $\phi = \phi_1 \cdot b_1/b \cdot p_1(p_1 + p_2) + \phi_2 \cdot b_2/b \cdot p_2/p_1 + p_2$  has been deduced, which applies to all cases.

J. F. S.

**Examination of Polányi's Theory of Adsorption.** LUDWIG BERÉNYI (*Zeitsch. physikal. Chem.*, 1920, **94**, 628–662. Compare A., 1916, ii, 474).—A theoretical paper in which a new method of calculating the partition of the adsorption potential in the adsorption space is developed. The method makes it possible to deduce this function from the isothermals of the adsorbed material above the critical temperature. This method has been applied to the adsorption isothermals of carbon dioxide, nitrogen, ethylene, carbon monoxide, methane, argon, and ammonia by charcoal, and sulphur dioxide and ammonia by silicic acid gels. The data used were obtained from the recent publications of Titoff (A., 1910, ii, 1041), Homfray (A., 1910, ii, 771, 1041), Richardson (A., 1917, ii, 526), and Patrick (Diss., Göttingen, 1914), and the results show that the demands of Polányi's hypothesis are moderately well fulfilled. The theory is applicable to the adsorption of vapours by silicic acid gels.

J. F. S.

**Adsorption as a Molecular Phenomenon. I.** NIKOLAI SCHILOV and LIDIE LEPIN (*Zeitsch. physikal. Chem.*, 1920, **94**, 25–71).—The adsorption of a very large number of electrolytes and other substances from aqueous, alcohol, acetone, and toluene solutions by wood charcoal has been determined. The charcoal used was activated by treatment with superheated steam and purified



by treatment with hydrochloric acid (1:1). The experiments show that adsorption is due to the forces and properties of undissociated molecules. The adsorbent takes part in the process not only by means of its electro-capillary forces, but also by virtue of the whole of its molecular forces. Consequently, adsorption is not to be treated only as capillary chemistry, but also as molecular chemistry. The phenomena of adsorption show themselves to be the more or less complicated result of the molecular forces of the adsorbent, the adsorbed material, and the solvent. The adsorbent exercises a definite field of force, which is dependent on the chemical properties of all the substances concerned in the process, and thereby it becomes to a certain extent specific. For the production of an energetic power of adsorption two conditions are necessary; a difference in structure and definite chemical properties of the adsorbent or its impurities, whereby, however, a chemical reaction need not necessarily be brought about. The molecular field of force of the adsorbent depends on its composition. The adsorption of electrolytes containing either a common anion or cation exhibits characteristic regularities: (1) A series of electrolytes of different cations with the same anion when arranged in groups according to the valency of the cation shows the influence of the atomic weight of the cation and a relationship to its position in the periodic system, in the sense that the adsorption is greater the greater the atomic weight. A further series of the cations may be made with respect to hydrogen, in which those which are more electropositive fall into one group and those which are less electropositive fall into the other. (2) A series of electrolytes of various anions and one cation can be arranged into a number of groups of similar adsorptive properties; it is found that similar types of compounds occur in the same group. The following order of adsorption is found:  $\text{H}_3\text{XO}_3 \rightarrow \text{H}_3\text{XO}_4 \rightarrow \text{H}_2\text{XO}_4 \rightarrow \text{HXO}_3 \rightarrow \text{HXO}_4$ . The halogen and organic compounds may also be more or less regularly fitted into the complete series. In each group of a definite type the influence of the relative weight of the anion on the order of the adsorption is clearly marked in the sense that the greater the weight of the anion the more strongly is the substance adsorbed. The adsorption from a mixture of two substances is specific for each pair; it is not directly connected with the degree of dissociation, and cannot be completely explained by the mutual replacement of the substances by one another in the solid phase. The mutual influence of substances on their adsorption shows itself in the liquid phase in consequence of the change in the number of molecules in the solution, due to the formation of solvates or complex molecules. Two cases have been observed: (1) mutual increase in the adsorption of both substances; (2) change in the amount of adsorption of one substance in the presence of a second, which is practically not absorbed at all, for example, the action of neutral salts on the adsorption of acids, alkalis, and other salts with similar ions. The rôle of the solvent in the adsorption process shows itself not only in its own adsorption, but it is of a much

more important and general nature. The solvent, by virtue of its field of force, acts with the adsorbent in the partition of the adsorbed substance between the solid and liquid phases. This view is confirmed from the adsorption from mixed solvents. Here two types of curves and adsorption are observed, which show the dependence of the adsorption on the composition of the binary mixture of solvents: (1) the adsorption shows a definite minimum for a fixed composition of the solvent; (2) all mixtures of two solvents have an adsorption value which is the mean of that of the components.

The adsorption processes have a close connexion with the solubility phenomena, and with some of the facts of chemical kinetics, generally with all those processes in which the concentration of the undissociated molecule exerts itself and in which the influence of neutral salts has been observed. All such phenomena are to be regarded as due to molecular fields of force. J. F. S.

**Retention of Gases by Solid Substances. I. and II. Experiments on Carbonyl Chloride.** DOMENICO LO MONACO (*Arch. Farm. sper. Sci. aff.*, 1920, 29, 3—47).—The preparation, properties, and uses of carbonyl chloride are described. The experiments made show that common materials, such as straw, hay, grass, soil, snow, fresh leaves, marine algae, sawdust, charcoal and cotton, are capable, especially if moist, of absorbing to some extent the asphyxiating gases used in warfare. T. H. P.

**Adsorptive Stratification in Gels. IV.** SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1920, 14, 474—482).—The formation of banded precipitates is due to adsorption of solute from the region between the bands. Only precipitates with great specific surface form bands. This factor is influenced by conditions, such as the reaction medium and the presence of ions. By varying its specific surface, a given substance may be obtained in a banded form or not, as desired; thus, by increasing the dispersity of silver chromate and dichromate, beautiful bands of both substances may be obtained in agar, a medium in which they do not usually form bands. J. C. D.

**Surface Tension of Vibrating Liquid Streams Investigated with Water and Aqueous Salt Solutions.** H. STOCKER (*Zeitsch. physikal. Chem.*, 1920, 94, 149—180. Compare Pedersen, A., 1908, ii, 158).—The surface tension of water and of solutions of sodium, potassium, magnesium, calcium, copper, zinc and ferrous sulphates, sodium, potassium, ammonium, calcium, barium and magnesium chlorides, potassium bromide, nitrate, chlorate and perchlorate, sodium chlorate, mercurio cyanide, ammonia, and sucrose has been determined by measuring the amplitude of the wave produced when a stream of the solution emerges from an oval capillary tube under pressure. In the case of water at 18° the surface tension for the vibrating stream is found to be  $72.43 \pm 0.15$  dyne/cm., whilst the accepted value for stationary water is  $72.94 \pm 0.12$  dyne/cm. In the case of

all the solutions examined except that of ammonia, the surface tension under these conditions is found to be somewhat greater than, or in the limiting cases equal to, that of water at the same temperature. J. F. S.

**Method of Determining Several Viscosities Simultaneously.** J. HOLKER (*J. Path. Bact.*, 1920, 23, 177—184).—The method of Scarpa (A., 1911, ii, 17) has been modified, and a method devised for determining several viscosities simultaneously. The method depends on the measurement of two times,  $t_1$  and  $t_2$ , the former occupied in drawing up through a vertical capillary sufficient liquid to fill a bulb at the top of this tube, and the latter taken by the liquid in flowing out of the bulb under its own weight. Under constant conditions, the viscosity is then proportional to  $t_1 t_2 / (t_1 + t_2)$ . J. R. P.

**Application of the Theory of Expansion Tension to the Study of Diffusion.** L. GAY (*J. Chim. physique*, 1920, 18, 103—125).—A mathematical discussion of the subject. W. G.

**Factors Affecting Rhythmic Precipitation.** ALFRED E. KOENIG (*J. Physical Chem.*, 1920, 24, 466—477).—A number of experiments are described which show that the uniformity of the bands formed in rhythmic precipitation is uninfluenced by the structure of the gels. This non-uniform structure may be brought about by keeping the gel for some time before the solution is poured on it or by pouring the mixture of sodium silicate and acid just before it sets. The bands of the precipitate may be modified by the presence in the gel of substances such as alcohols, carbamide, and sucrose, all of which modify the rates of diffusion of the reacting substances and the solubility of the precipitated products. The rhythmic bands may be broken up more or less by the presence in the gel of various inert powders unevenly distributed and by the presence of small particles of soap, all of which tend to interfere with the uniform diffusion of the reacting substances. A series of experiments on the formation of rhythmic bands by the interaction in narrow tubes of such gases as ammonia with hydrogen chloride, bromide, or fluoride, and hydrogen sulphide with chlorine or sulphur dioxide has been described, and the relationship with similar reactions in gels pointed out. In addition to the effects of diffusion and the factors that modify it, there are also the effects of the concentrations necessary for precipitation to take place, the velocity of the reaction which forms the precipitate and the degree of supersaturation which the resulting substance may reach in a given medium, before precipitation takes place. J. F. S.

**Diffusion and Mobility of Cobalt and Nickel Ions.** ELISABETH RONA (*Zeitsch. physikal. Chem.*, 1920, 95, 62—65).—The diffusion constant,  $D$ , for cobalt chloride and nickel nitrate in aqueous and acid solutions has been determined by the method previously described (A., 1917, ii, 286), and the following values

obtained at 18°: cobalt chloride, in aqueous solution, 0.0127*N*,  $D=0.669$ ; in 0.1*N*-hydrochloric acid solution, 0.1*N*,  $D=0.634$ ; in 0.01*N*-hydrochloric acid solution, 0.01*N*,  $D=0.882$ ; nickel nitrate, in aqueous solution, 0.068*N*,  $D=0.802$ ; in 0.1*N*-nitric acid solution, 0.0413*N*,  $D=0.646$ ; in 0.01*N*-nitric acid solution, 0.0108*N*,  $D=0.719$ . In aqueous solution and in dilute acid solution the value of  $D$  decreases with decreasing salt concentration, but increases with decreasing concentration in the more concentrated acid solutions. As the solutions become more dilute the value of  $D$  approaches a limiting value which is the value of the bivalent ion. From these values, making use of the formulae  $u=Dv/(0.0224v-D)$  and  $u=2D/0.0224$ , the mobility of the bivalent ions has been calculated and the values Ni=48.0 and Co=47.7 obtained. J. F. S.

**Diffusion Experiments with Highly Active Saccharase Preparations.** H. VON EULER, A. HEDELIUS, and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1920, 110, 190--216).—Diffusion experiments with different saccharase preparations have given velocities of diffusion of varying magnitudes, and consequently the calculated molecular weights also showed significant variations. The authors conclude that the substrate and the products of the enzymic action do not diminish the size of the colloidal particles of the saccharase, and the velocity of diffusion at the optimum acidity required for the action of the enzyme is not essentially different from that in water. S. S. Z.

**Permeability of Thin Fabrics and Films to Hydrogen and Helium.** J. C. McLENNAN and W. W. SHAVER (*Phil. Mag.*, 1920, [vi], 40, 272--280; see Elworthy and Murray, this vol., ii, 508).—The rate of diffusion of hydrogen through a series of balloon fabrics has been determined. The permeability of soap films of thickness corresponding with the reddish-green stage is, for helium, 670 litres per sq. m. per day, and for hydrogen 960 litres per sq. m. per day, at 20°. The rate of transfusion of helium through soap films is 0.70 times that for hydrogen through similar films. The diffusion of hydrogen through water films filling the interstices of wet cotton fabric is very low. J. R. P.

**Anomalous Osmosis of some Solutions of Electrolytes with Gold-beater's Skin Membranes.** F. E. BARTELL and O. E. MADISON (*J. Physical Chem.*, 1920, 24, 444--465).—The osmotic effects of a number of solutions with gold-beater's skin have been examined with the object of ascertaining whether any parallelism exists between the observed effects and the potential difference associated with the same combination. In the case of sucrose it is shown that the rate of osmosis is very nearly proportional to the concentration of the solution. The direction and the magnitude of the flow of solution are, in practically every case, exactly those which would be predicted. If the solution side of the membrane

is of the same electrical sign as the capillary liquid layer the resulting osmosis will be abnormally low or negative, whereas if these parts of the system are of opposite sign the resulting osmosis will be abnormally high. With salts of univalent and bivalent cations the superimposed effect is found to work in opposition to the normal osmosis, with the result that the observed rate of osmosis is less than normal. With salts of aluminium and thorium the superimposed effect works in conjunction with the normal osmosis, and the result is an abnormally large osmosis. Increase in concentration causes but slight increase in the osmosis of solutions of univalent cations, a marked decrease in the osmosis of solutions of bivalent cations and a decidedly greater increase in the osmosis of solutions of trivalent and quadrivalent cations. A logical explanation of the facts seems to be that with dilute solutions of univalent and bivalent cations, the charges of the membrane against the solution is at all times electronegative, which tends to produce an abnormally low osmosis. In the case of solutions of bivalent cations there is a marked tendency to neutralise the negative charge of the membrane, with the result that with more concentrated solutions the membrane approaches the isoelectric point and osmosis now approaches the normal rate. In the case of solutions of trivalent and quadrivalent cations, the sign of the membrane is positive, even with very dilute solutions; this results in an abnormally large positive endosmosis in every case. With two-compartment cells, the concentrations of the solutions on the two sides of the membrane are much more nearly equal than in the one-compartment cell. This is due to the small initial water volume, with the result that the *E.M.F.* of the membrane system is, in this case, much less than in the case of the one-compartment cell. Owing to the smaller potential difference between the two faces of the membrane, the resulting osmosis is in all cases more nearly normal. In the case of solutions of univalent cations, there exists a smaller tendency to negative osmosis, whereas in the case of solutions of multivalent cations, such as thorium and aluminium, there exists a smaller tendency for an abnormally great positive osmosis. In the case of dilute acid the tendency is toward an abnormally great positive osmosis. As the concentration of the acid is increased, the sign of the capillary system is reversed, and the osmotic tendency passes from abnormally great positive to normal, and then to abnormally small, and finally to negative osmosis. In the case of sodium hydroxide a negative tendency persists throughout. At the higher concentrations the electrical factors of the system are such that negative osmosis results. Porcelain membranes yield similar results with acids and alkalis.

J. F. S.

**Thermodynamics of Mixtures. I.** MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **94**, 592-627).—A mathematical paper in which the equilibrium and reversibility conditions are deduced for purely physical and physicochemical mixtures.

J. F. S.

**Thermodynamics of Mixtures. II. and III.** MARIO BASTO WAGNER (*Zeitsch. physikal. Chem.*, 1920, **95**, 15—36, 37—61. Compare preceding abstract).—A mathematical paper in which expressions are developed in connexion with the osmotic pressure of solutions of any concentration. The volume of mixtures is considered as a function of the volumes of the components and the heat of mixture. Four methods of calculating the degree of association of anomalous substances are deduced, and expressions for calculating the heat of mixing are developed. J. F. S.

**The Solubility of Acraldehyde in Water and of Water in Acraldehyde at Different Temperatures.** A. BOUTARIC (*J. Chim. Phys.*, 1920, **18**, 126—132).—The author has measured the solubilities of water in acraldehyde and of acraldehyde in water over the temperature range  $-10^{\circ}$  to  $+50^{\circ}$ . The presence in acraldehyde of such substances as quinol or gallic acid, used to stabilise it, causes a diminution in the solubility of acraldehyde in water and an increase in the solubility of water in acraldehyde. W. G.

**Ionic Radius and Ionic Efficiency.** JACQUES LOEB (*J. gen. Physiol.*, 1920, **2**, 673—687).—It has been shown previously that when solutions of electrolytes are separated from pure water by collodion membranes, the ions with the same sign of charge as the membrane increase, whilst the ions with the opposite sign of charge diminish, the rate of diffusion of water from the side of pure water to the side of solution, and that the accelerating and depressing effects of these ions on the rate of diffusion of water increase with their valency. It is now found that, aside from the valency, a second quantity of the ion plays a rôle in this effect, namely, the radius, which in a monatomic ion means the distance between the central positive nucleus and the outermost ring or shell of electrons of the ion. In monatomic, univalent anions the radius increases in the order  $\text{Cl} < \text{Br} < \text{I}$  (being largest in I), whilst for monatomic, univalent cations it increases in the order  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$  (being largest in Rb). The accelerating as well as the depressing effect of the anions mentioned increases directly with the order of magnitude of their radius, and the efficiency is greatest in the case of iodine, which has the largest radius; the accelerating as well as the depressing effect of the cations increases inversely with the order of magnitude of their radius, lithium with the smallest radius having the greatest efficiency. This is intelligible on the assumption that the action of the ions is electrostatic in character, in the case of cations due to the electrostatic effect of the excess charge of their positive nucleus, and in the case of anions due to the excess charge of their captured electron. The electrostatic effect of the positive nucleus of a cation on the membrane (or any other body) will be the greater the smaller the ionic radius of the cation; and the electrostatic effect of an excess electron will be the greater the further its distance from its own positive nucleus. It is suggested that this rule

may possibly include polyatomic, univalent ions (such as  $\text{NO}_3$ ,  $\text{CNS}$ , etc.) if these are replaced by monatomic models in which the radius is calculated in such a manner as to give the model the same electrostatic effect which the polyatomic ion possesses. These conclusions are in harmony with the fact that the efficiency of ions increases also with their valency. It is suggested that these rules concerning the influence of the ionic radius can possibly be demonstrated in other phenomena, depending on the electrostatic effect of ions.

H. W.

**Relationship between the Non-dissociated Part  $(1-\alpha)$  of Dissolved Salts and the Dielectric Constant  $\epsilon$  of the Solvent.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 374—404).—From a consideration of a large amount of experimental data it is shown that for a salt in a given solvent the product  $(1-\alpha) \sqrt[3]{v}$  is constant over a wide range of dilution, that is,  $(1-\alpha) \sqrt[3]{v} = \text{const.}$ , or  $(1-\alpha) = \text{const.} / \sqrt[3]{v} = \text{const.} \cdot c^{1/3}$ . The undissociated portion of the electrolyte  $(1-\alpha)$  is therefore directly proportional to the linear concentration  $c^{1/3}$ , or the distance between the molecules in the solution. The constant  $(1-\alpha) \sqrt[3]{v} = K$  is practically the same for different typical binary salts in every solvent, provided that the electrolytes are about equally strong in aqueous solution; this constant is characteristic for the binary salts examined, and fluctuates only slightly about a mean value. When the dielectric constant is taken into account, a constant value is obtained which is fundamental to the above-mentioned constant, and this applies to solvents of the most widely differing character; this constant is represented by  $(1-\alpha) \cdot \epsilon \cdot \sqrt[3]{v} = \text{const.} \sim 41.5$ , or  $(1-\alpha) \sim \text{const.} \cdot c^{1/3} / \epsilon$ , that is, in different solvents the undissociated portion of the electrolyte is almost directly proportional to the linear concentration,  $c^{1/3}$ , and indirectly proportional to the dielectric constant,  $\epsilon$ , of the solvent.

J. F. S.

**Some Thermodynamical Formulae.** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1920, **94**, 739—762).—A mathematical paper in which it is shown that the van't Hoff reaction isothermal, which is based on the well-known osmotic pressure equation, for dilute solutions assumes in its derivation that for changing concentration the total pressure changes in such a way that the partial pressure of the solvent remains constant. Consequently, the isothermal does not refer strictly to constant volume relationships. This reaction isotherm, from its kinetic derivation, appears to be applicable for constant volume relations, but strictly it is for this purpose only an approximation formula. The strictly developed reaction isotherm of Planck, which is based on the additivity of the volume and internal energy of dilute solutions, is different from that of van't Hoff, and leads to a different law for osmotic pressure, which agrees better with experimental observations than that of van't Hoff, and therefore is to be preferred. There is practically an objection to this formula, for it

contains the molecular fraction, and in the case of associated solvents, for example, water, the fraction is not accurately known. The Helmholtz equation,  $T(d\Delta A/dT)_v = \Delta U + \Delta A$ , is true, not only for constant volume, but also when isothermal processes at various temperatures are carried out in such a way that the change in volume remains the same. If the same isothermal process at different temperatures is carried out in such a way that the change in pressure remains exactly the same, the formula  $(d\Delta A/dT)_p = d\Delta p/dT + (\Delta U + \Delta A)/T$  holds. For complete equilibrium, these formulae are not applicable. In this case, the equation  $d\Delta A/dT = p d\Delta v/dT + (\Delta U + \Delta A)/T$  is applicable. On the basis of the Nernst theorem, a vapour-pressure formula is deduced in which the only approximation made is that the vapour is treated as an ideal gas. On the basis of this formula, equations are developed for the equilibrium constants in gas reactions and for the dependence of the heat of vaporisation on the temperature.

J. F. S.

**Relationship between the Electrolytic Dissociation and the Dielectric Constant of Solvents.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 263—294).—Making use of ionisation data previously obtained by the author (A., 1906, ii, 149) and by other investigators, by means of which it was shown that  $\epsilon^{1/3}/v = \text{constant}$ , it is now shown that all these practically equally strong salts in many solvents at the same dissociation step  $\alpha' = \alpha'' = \text{const.}$ , and the corresponding dilution,  $v$ , completely fulfil the equation  $\epsilon^{1/3}/v = \text{const.}$  The degree of dissociation has the value  $\alpha' = 0.50$ ,  $\alpha'' = 0.666$ , and in the third case,  $\alpha''' = 0.86$ , the dilution varied; for example, with constant degree of dissociation  $\alpha''' = 0.86$ ,  $v$  varied between 16 and 8000 litres. The Ostwald constant,

$$K_0 = \alpha^2/(1-\alpha)v,$$

has been calculated for the same degree of dissociation in all solvents; by combining these two equations, the expression  $\epsilon^{1/3}/K_0 = \text{constant}$  is found for a given  $\alpha$  value in all solvents, or the Ostwald constant,  $K_0 = \epsilon^3 \cdot \text{const.}$ , where  $\epsilon$  is the dielectric constant of the solvent. For infinite dilution,  $v = \alpha$ .  $\alpha = 1.00$  const., and  $K_0 = (0.0054\epsilon)^3$ . The dissociation constant for the typical strong binary salts in any solvent can be calculated by means of the equation for the condition when  $\alpha = 1.0$ . The values thus obtained agree in many cases exactly, and in others very nearly, with the experimentally determined values. For one and the same salt, tetrapropylammonium iodide, the value of  $K_0$  varies from 0.14 in formamide and hydrogen cyanide to 0.0000017 in benzene and carbon tetrachloride, or approximately in the ratio 100000:1. The cause of the decrease in the Ostwald constant with increasing dissociation is probably to be found in the fact that in a given solvent this deviation from the law of mass action is approximately proportional to the concentration of the undissociated salt, that is, for different  $\alpha$ -values,

$$K_0' : K_0'' : : (1-\alpha') : (1-\alpha''),$$

or  $K_0/(1-\alpha) = \text{const.} = K_0'$ . Transforming this to different solvents,

$$\epsilon^{1/3}/K_1 \sim \text{const.} \sim 78.$$

J. F. S.



**Molecular Condition of Binary Salts in Weakly Ionising Solvents. Solvation and Polymerism.** P. WALDEN (*Zeitsch. physikal. Chem.*, 1920, **94**, 295—373).—The author has examined the condition of binary salts in weakly ionising solvents by means of data previously published by the author himself and others, and also certain other fresh data now published. It is shown that solvolytic dissociation, as well as polymerisation of the dissolved molecules, are common phenomena in non-aqueous solutions. Both phenomena occur simultaneously, particularly in solvents with small dielectric constants, or one and the same solvent can promote a far-reaching solvolysis and a high degree of polymerisation. Acetic acid is a solvent which favours polymerisation. The highest degree of solvolysis is found in media which are practically insulators, such as naphthalene, benzene, carbon disulphide, and chlorinated hydrocarbons, and consequently the solvolytic dissociation cannot depend on ion formation or ion action. The degree of solvolysis of different salts of a common acid is influenced by (a) the strength of the base in the salt, and (b) the affinity of the medium towards one component of the salt, that is, the power of the solvent to form molecular compounds with the acid or base of the salt. One and the same salt can, according to the solvent, show all possible degrees of polymerisation; the degree of association,  $x$ , of its molecules can vary between  $x = \infty$  and  $x < 1$ , and here the dielectric constant of the solvent,  $E$ , plays the determining rôle; the degree of association is greater the smaller the value of  $E$ . Quantitatively, it is found for similar degrees of association  $x_1 = x_2 = \text{constant}$  in various solvents the dielectric constants of which are  $E_1, E_2, E_3$ , and the corresponding dilutions  $v_1, v_2, v_3$  that the expression  $E_1 \sqrt{x_1} = E_2 \sqrt{x_2} = \text{constant}$ , holds. When this expression is re-formed for different degrees of association, the general approximate expression  $x \cdot E \sqrt{v} = \text{const} \sim 36$  is obtained. Since these relationships between the degree of depolymerisation of salt molecules and the dielectric constant,  $E$ , of the solvent are exactly the same as those between the electrolytic dissociation of the same salt molecules in ionising solvents, it follows that it is likely that depolymerisation occurs according to the scheme

J. F. S.



**Structure of Precipitates.** SVEN ODÉN (*Svensk. Kem. Tidskr.*, 1920, **5**, 74—85; from *Chem. Zentr.*, 1920, iii, 223). The author has drawn conclusions as to the structure of precipitates from microscopical investigation and determination of the velocity of sedimentation by the continuous weighing of the sediment falling on a metal plate placed at the bottom of the solution. From sufficiently supersaturated solution, primary particles of the magnitude  $1 \mu - 10 \mu$  are initially formed, which only remain unchanged in exceptional cases. In general, secondary aggregates are further formed, which sink rapidly; these aggregates can frequently be disintegrated by agitation. The author develops

the relationship between the amount of precipitate which has fallen to the bottom and the time by a series of graphs (accumulation graphs), and distinguishes types of reversible and irreversible aggregation. The irreversible aggregates grow continuously, whilst the reversible ones attain a maximal magnitude for which an aggregation period can be found. The influence of the concentration of the electrolyte on the time of aggregation is in harmony with the investigation of Westgren (this vol., ii, 99). The alteration in the time of aggregation with the number of particles was investigated for a constant electrolyte content at the instance of the precipitation of barium sulphate in the presence of citric acid as coagulator, and the results are in agreement with von Smoluchowski's coagulation formula (A., 1917, ii, 297). The cause of the formation of secondary aggregates lies in capillary and adhesion forces, which bring about the coagulation of the colloidal particles. The size of the aggregates increases as the difference in potential between the particles and the liquid diminishes. It has been found possible, under perfectly definite conditions, to calculate the number of primary particles in an aggregate for a suspension of barium sulphate with citric acid as electrolyte. Aggregation and disaggregation have been investigated with increasing additions of this electrolyte.

H. W.

**Retardation of Crystallisation in Supersaturated Solutions.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 482—504).—The relationship of the solubility of cadmium iodide to pressure has been examined at 30°, and the relationship between the volume and concentration found to be given by the expression  $v_s = 1.00435 - 0.820924c + 0.016857c^2$ . The crystallisation of saturated solutions has also been studied, and it is shown that strongly supersaturated solutions may, even in the presence of the solid phase, be caused to crystallise very slowly, in consequence of the presence of small quantities of a third substance. The saturation concentration may apparently, and very slowly, be overstepped at a given concentration in the presence of a small quantity of a third substance.

J. F. S.

**Symmetry of the Röntgen Patterns obtained by means of Systems Composed of Crystalline Lamellæ, and the Structure of Pseudo-symmetrical Crystals.** F. M. JÄGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **22**, 815—830).—Röntgen patterns have been obtained by passing the rays through plates of muscovite (0.32 mm. thick) which crossed one another at various angles (45° or 60°). The patterns obtained indicate that if the central part of a regular complex of crystalline lamellæ, cut perpendicular to a plane of symmetry of the crystals, and crossing at angles  $\alpha = 2\pi/n$ , be radiated by Röntgen rays, the normal diffraction pattern thus obtained will exhibit an axis of  $n$ -fold symmetry, showing, therefore, the image of the original pattern repeated  $n$  times. The diffraction image of the dextro-

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and lævo-rotatory complexes of this kind are always identical. Reproductions of photographs of the patterns obtained are given in the paper.

J. F. S.

### **Bragg's Work and the Law of Definite Proportions.**

A. QUARTAROLI (*Gazzetta*, 1920, 50, ii, 60—64).—From the investigations of Bragg on crystals of sodium chloride and analogous compounds, diamond, pyrites, etc., it follows that such crystals represent a homogeneous mixture of atoms distributed regularly in space. For instance, in the case of iron pyrites, the elementary cube has four atoms of iron at alternate corners and an atom of sulphur in the interior. An aggregation of  $n^3$  such cubes has the composition  $\text{Fe}_{n+1}^{10}\text{S}_{2n+5}$ , which approximates to  $\text{FeS}_2$  when  $n$  is very large, but when  $n$  is 50 and the aggregate of the order of magnitude of granules visible by the ultramicroscope, the composition is represented by the formula  $\text{FeS}_{1.885}$ . It is therefore possible that continuous variations may occur in the chemical composition of micro-crystals in accordance with the magnitude of such crystals when deposited; with pyrites, the composition might vary from  $\text{Fe}_4\text{S}$  to  $\text{FeS}_2$ .

T. H. P.

### **The Reversal of the Sign of the Charge of Colloidion Membranes by Tervalent Cations.**

JACQUES LOEB (*J. gen. Physiol.*, 1920, 2, 659—671).—Tervalent cations cause a colloidion membrane covered with a protein film to be charged positively, whilst they do not produce such an effect on colloidion membranes not possessing a protein film. The same has been found for the reversal of the sign of charge of the membrane by acid. This reversal in the sign of charge of the membrane by tervalent cations occurs on the alkaline side of the isoelectric point of the protein used, whilst the reversal by acid occurs on the acid side of the isoelectric point. The reversal seems to be due to, or to be accompanied in both cases by, a chemical change in the protein. The chemical change which occurs when the hydrogen ions reverse the sign of charge of the protein film consists in the formation of a protein-acid salt, whereby the hydrogen ion becomes part of a complex protein cation, whilst the change which takes place when tervalent cations reverse the sign of charge of the protein film consists in the formation of an insoluble, and therefore sparingly or non-ionisable, metal proteinate.

H. W.

### **A Series of Abnormal Liesegang Stratifications.**

EMIL HATSCHKE (*Biochem. J.*, 1920, 14, 418—421).—A number of such abnormalities, which were encountered when attempts to obtain stratification of calcium phosphate in gelatin were made, are described and illustrated. It is obviously impossible to attempt an explanation of these abnormal results in the present unsatisfactory state of knowledge regarding the normal phenomenon.

J. C. D.

### **Application of Smoluchowski's Equation to the Change with Time of the Number of Particles in an Emulsion.**

P. C. VON ARKEL (*Physikal. Zeitsch.*, 1920, 21, 465—467).—According-

ing to Smoluchowski (see A., 1916, ii, 302), the formula deduced by him for the Brownian movement is in agreement with the observations of Svedberg ("Existenz der Moleküle," 1912, p. 148). It is shown that this agreement is not sufficiently close when all the deductions of Smoluchowski are compared with the experimental numbers. The differences are probably to be explained by the incompleteness of the series of observations rather than by defects in the theory.

J. R. P.

### Conductivity Depression and Adsorption by Lyophile Colloids. M. POLANYI (*Biochem. Zeitsch.*, 1920, 104, 237—253).

—The name "L-effect" is given to the percentage by which the electrical conductivity of a mixture of electrolyte and colloidal solution falls short of that of the colloid-free disperse medium of the same mixture; the specific L-effect refers to 1 gram of dissolved colloid. Whereas crystalloids lower the conductivity in the same measure as they raise the viscosity of the solvent, colloids depress the conductivity far less than the fluidity; this discrepancy indicates that the ions in colloidal solutions set in motion only the disperse medium, and not, to any extent, the colloidal particles.

The method employed to measure the L-effect consists in leaving a parchment thimble containing a colloidal solution immersed in a definite quantity of water until the diffusion reaches a condition of equilibrium, and then measuring the electrical conductivities of the colloidal solution remaining inside the thimble and of the pure, disperse medium from the outer vessel. The results thus obtained with various colloids and electrolytes are given, and calculations made of the "non-conducting space," that is, the volume per gram of colloid calculated on the assumption that the colloidal particles, by their mere presence, diminish the number of ions per c.c. and prolong their paths. This assumption almost suffices to account for the magnitudes found for the L-volume.

The swelling of colloidal substances indicates that part of the disperse medium is held by the colloidal particles, and the assumption may be made that the small amounts by which the non-conducting space exceeds the specific volume of colloidal substances, namely, 0.8, have their origin in the increase in size of the colloidal particles caused by the aqueous envelope. Explanations of the depression of the conductivity of electrolytes by colloids other than the purely mechanical one appear to be excluded by the following observations: (1) The L-effect of casein is the same when the casein is dissolved as sodium caseinate as when it is simply suspended in the coarsely granular, undissolved condition. (2) The L-effect is, within wide limits, proportional to the concentration of the colloid. This hypothesis assumes that all the ions in an electrolyte are influenced to the same extent by a colloid, but since Cybulski and Kunin-Borkowski (*Krak. Anz.*, 1909, 660) have found that the transport numbers are altered considerably by the presence of colloids, the author makes the further assumption that the aqueous envelopes of the colloidal particles are permeable to varying degrees

for different ions; this assumption also serves to explain the effect of the colloid on the diffusion potential.

The adsorption of electrolytes in colloidal solution is also considered, use being made of the equilibrium dialysis to determine the "non-dissolving space," that is, the space taken up by the colloid. If the specific volume of the colloid is 0.8, positive or negative adsorption is shown by the non-dissolving space per gram of colloidal substance being smaller or larger than 0.8. It has been shown thermodynamically that substances which increase (or diminish) the osmotic pressure of colloids are adsorbed positively (or negatively) (A., 1914, ii, 720). Since continued diminution of the osmotic pressure must lead finally to coagulation, the obvious conclusion is that coagulating substances must be negatively, and those which hinder coagulation positively, adsorbed. This conclusion requires experimental proof, but is supported by the fact that dextrose, which retards the coagulation of albumin considerably, is positively adsorbed by albumin to a marked extent.

T. H. P.

**Undamped Oscillations derived from the Law of Mass Action.** ALFRED J. LOTKA (*J. Amer. Chem. Soc.*, 1920, 42, 1595-1599). - A theoretical paper in which it is shown that in certain circumstances conditions may be obtained in an homogeneous system for the production of undamped oscillations in the absence of any geometrical cause.

J. F. S.

**Statistical Meaning of the Thermodynamical Functions** KARL F. HERZFELD (*Zeitsch. physikal. Chem.*, 1920, 95, 139-153). - A mathematical paper in which a number of statistical formulae are discussed and the difference between the external work and the added heat pointed out. The dependence of the total energy on the temperature is discussed. Using the same formulae, the conditions of chemical equilibria and chemical potential for gaseous and dilute solution systems are developed. The equations deduced in the last cases are then applied to the formulae of von Laue.

J. F. S.

**Temperature-coefficients of the Action of Saccharase.** HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1920, 110, 55-92). Determination of the velocities of inversion by saccharase at pairs of different temperatures shows that the constant  $A$  of Arrhenius's temperature formula (this vol. i, 506) varies with the temperature in accordance with the equation  $A = 11,409(1 - 0.0094)$ , which is in agreement with the results of Kjeldahl (A., 1883, 225) and O'Sullivan and Tompson (T., 1890, 57, 834).

There is no theoretical basis indicating the independence of the constant  $A$  on the temperature; according to Arrhenius (A., 1889, 1103),  $A$  represents the heat change of the reaction, and there is no reason to assume that this heat change must always be independent of the temperature. On the other hand, the

Arrhenius temperature formula agrees well with the experimental results over a wide range of temperature, especially for the inversion of sucrose by acids. On the assumption that the velocity of the enzymic inversion of sucrose is proportional to the concentration of the complex molecule, sucrose-enzyme, the temperature-coefficient of the inversion is determined by the following magnitudes: (1) the influence of the temperature on the concentration of the active enzyme; (2) the influence of the temperature on the reactivity of the compound, sucrose-enzyme (and the reactivity of the water); and (3) the alteration of the equilibrium, sucrose: enzyme, with temperature. The last of these may be determined quantitatively on the basis of Michaelis and Menten's theory (A., 1913, i, 540), according to which  $[S][E - \phi] = K[\phi]$ , where  $[S]$  is the concentration of the free substrate,  $[E]$  the total molar concentration of the enzyme,  $[\phi]$  the concentration of the combined enzyme or of the compound, sucrose-enzyme, and  $K$  the equilibrium constant. The value of the velocity of inversion is given by  $v = C[\phi] = C[E][S]/([S] + K)$ ,  $C$  being a proportionality factor; influence (2) is expressed in the factor  $C$  and influence (3) in  $K$ .

The authors have measured the values of the constant  $K$ , of the equilibrium between sucrose and enzyme for the temperature interval 0–40°, use being made of methods essentially the same as that of Michaelis and Menten (*loc. cit.*). At 25° and for the optimal acidity ( $p_H = 4.5$ ), the value of  $K$  is found to be  $26.10^{-3}$ , which remains unchanged over the acidity region  $p_H = 3.35-5.65$ ; the above authors gave  $16.10^{-3}$ . Three-fold increase of the concentration of the enzyme is without influence on the value of  $K$ .

The equilibrium constants of the equilibrium  $[S][E - \phi] = K\phi$ , obtained for the temperatures 1°, 15°, 25°, and 39°, show that the equilibrium is altered approximately by 1% per degree rise of temperature; the values obtained at these temperatures agree well with those calculated with the help of the heat of dissociation,  $Q$ , this being found by the equation  $Q = -RT^2 \cdot d \log k / dT = -[4.58(\log K_2 - \log K_1)T_1T_2] \cdot (T_2 - T_1)$  to have the mean value 2000 cal.

As regards the great difference between the temperature-coefficients for enzymic inversion (9400 at 20°) and acid inversion (25,600 at 20°), the results obtained show that this is not due to abnormal alteration of the equilibrium enzyme:sucrose, but that it can depend only on increase in concentration of the compound, sucrose-acid, as the temperature rises.

T. H. P.

#### Ester Formation in Absolute Ethyl Alcohol. HEINRICH

GOLDSCHMIDT, J. ANDERSON, M. FEIGL, G. GÖRBITZ, J. SCHJERVE, J. SVENDSEN, A. TRUESEN, O. UDBY, and P. WRAA (*Zeitsch. physikal. Chem.*, 1920, **94**, 233–253).—The rate of esterification of acetic acid in absolute alcohol has been determined with trichlorobutyric, trichloroacetic, picric, hydrochloric, and sulphobutylic acids as catalysts. Similar experiments with the same

catalysts have been carried out for the rate of esterification of propionic, *n*-butyric, isobutyric, *n*-valeric, isovaleric, pivalic, heptic, phenylacetic, phenylpropionic, and glycollic acids. The results in all cases show that the rate of esterification is satisfactorily represented by the formula  $k = c[K_A\gamma + K_B(1-\gamma)]$ . The results also show that both the ions and the undissociated acid act catalytically. The velocity-constant for the undissociated portion of the catalyst,  $K_B$ , is in general the greater the greater the affinity-constant of the catalyst. The relationship of  $K_A$ , the velocity-constant of the reaction catalysed by the hydrogen ions, to  $K_B$  is in general, for the different acids with one and the same catalyst, not constant. The relationship  $K_A/K_B$  in the case of hydrochloric acid as catalyst is not equal to unity, but considerably greater, in all cases investigated. For calculating the present results, the degree of dissociation of picric acid was necessary. This has been obtained from electro-conductivity determinations of aniline picrate in alcohol solution. The value  $\lambda_\infty = 49$  is obtained. The values of  $K_A$  and  $K_B$  are given for all cases examined. J. F. S.

**Formation and Hydrolysis of Lactones.** A. KAILA (*Zeitsch. physikal. Chem.*, 1920, **94**, 111—128).—A theoretical paper in which the experimental results of P. Henry (A., 1892 ii, 1303) on the rate of formation of the lactones of  $\gamma$ -hydroxybutyric acid and  $\gamma$ -hydroxyvaleric acid have been recalculated. It is shown that, in the above-named reactions in aqueous solution with strong acids as catalysts, the catalytic action of the undissociated acid, if it is present at all, is in any case much smaller than that of the hydrogen ion. The velocity-coefficients have been calculated for the experiments of Johansson and Sebelius (A. 1918, ii, 223) on the hydrolysis of  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone with nitric acid as catalyst, and it is shown that here also the velocity of the reaction is proportional to the concentration of the hydrogen ion rather than to that of the total acid. The demands of the theory, that, starting from either the hydroxyacids or the lactones, the same value must be obtained for the sum of the constants of the velocity of hydrolysis or lactone formation, are fulfilled within the possible experimental error. The apparent contradiction, furnished by Henry's results on lactone formation with acetic acid as catalyst and also without catalyst, to the hypothesis of a pure hydrogen-ion catalysis can be, to a large extent, brought into line with this hypothesis by the assumption that most of the products used by Henry contained small amounts of silver salts from their preparation. This leaves out of consideration the action of the undissociated molecule, if such exists. J. F. S.

**Quantitative Kinetic Analysis in the Case of Bimolecular Reactions.** L. SWERN (*Zeitsch. physikal. Chem.*, 1920, **95**, 66—94).—The kinetics of reactions of mixtures are discussed theoretically with the object of deducing methods by which the composition of a mixture of two allied and difficultly separable substances may

be ascertained from the velocity-constant of a reaction carried out with the mixture and a given reagent, such as the rate of hydrolysis of a mixture of esters with alkali hydroxide. Two methods are elaborated, the first, a graphic method which is applicable when the reaction-constants of the pure components, as well as that of the mixture, are all known, and the second, a mathematical method applicable when the reaction-constants for the mixture and one component are known, and when one of the components reacts much more rapidly than the other. The methods are applied to the reaction of barium hydroxide on mixtures of  $\alpha$ - and  $\beta$ -glyceryl chlorohydrin and to the hydrolysis of a mixture of ethyl butyrate and acetate by the same reagent. The results show the value and trustworthy character of both methods.

J. F. S.

#### Ageing of Colloidal Catalysts (Platinum, Palladium).

GREGORIO DE ROCASOLANO (*Compt. rend.*, 1920, 171, 301—303).—The catalytic activity of electrosols of platinum and hydrosols of palladium increases at first with age until it reaches a maximum, and then decreases.

W. G.

#### Influence of the Substrate Concentration on the Rate of Hydrolysis of Proteins by Pepsin.

JOHN H. NORTHRUP (*J. gen. Physiol.*, 1920, 2, 595—611).—It is pointed out that the apparent exceptions to the law of mass action found in enzyme reactions are also encountered in catalytic actions in strictly homogeneous solutions. These deviations may be explained by the hypothesis that the active mass of the reacting substances is not directly proportional to the total concentration of substance taken. In support of this suggestion, it is shown that for any given concentration of pepsin the relative rate of digestion of concentrated and of dilute protein solutions is always the same. If the rate of digestion depended on the saturation of the surface of the enzyme by substrate, the relative rate of digestion of concentrated protein solutions should increase more rapidly with the concentration of enzyme than that of dilute solutions. This is found not to be true, even when the enzyme could not be considered saturated in the dilute protein solutions.

The rate of digestion and the conductivity of egg-albumin solutions of different concentration are found to be approximately proportional at the same  $P_H$ . This agrees with the hypothesis first expressed by Pauli, that the ionised protein is largely or entirely the form which is attacked by the enzyme. The rate of digestion is diminished by a very large increase in the viscosity of the protein solution; this effect is probably mechanical in nature and due to the retardation of the diffusion of the enzyme.

H. W.

#### Catalysis with Platinum Black. II. E. OLIVERI-MANDALA

(*Gazzetta*, 1920, 50, ii, 81—89. Compare A., 1916, ii, 615).—According to Traube's hypothesis, the function of platinum black in the catalysis of hydrogen peroxide is represented by the equa-



tions:  $n\text{Pt} + y\text{H}_2\text{O}_2 = \text{Pt}_n\text{O}_y + y\text{H}_2\text{O}$  and  $\text{Pt}_n\text{O}_y + y\text{H}_2\text{O}_2 = n\text{Pt} + y\text{H}_2\text{O} + y\text{O}_2$ . This hypothesis scarcely seems capable of extension to the catalyses of ammonium nitrite, azoimide, hydroxylamine, and hydrazine, represented by the respective equations  $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$ ,  $3\text{N}_2\text{H}_4 = 4\text{N}_2 + \text{NH}_3$ ,  $4\text{NH}_3\text{O} = 2\text{NH}_3 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ , and  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ , especially when the absence of oxygen from azoimide and hydrazine is considered. It may be that the catalyst reacts with water, forming a platinum oxide and hydrogen, catalytic oxidations and reductions being thus rendered possible. In this way, it is possible to explain the different steps in the three different catalytic decompositions of hydrazine, namely, (1)  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{H}_2 + \text{N}_2$ , (2)  $3\text{N}_2\text{H}_4 = \text{N}_2 + 4\text{NH}_3$ , and (3)  $3\text{N}_2\text{H}_4 = 2\text{N}_2 + 2\text{NH}_3 + 3\text{H}_2$ .

A similar explanation may be given for the catalysis of hydroxylamine by platinum black (Tanatar, A., 1902, ii, 386, 495). The equation given above indicates a reaction of the fourth order for this decomposition, but the author's study of the velocity shows that the reaction is of the first order, and that it is the result of a number of simple reactions.

The mechanisms of the catalyses of azoimide (Cooke, P., 1903, 213) and ammonium nitrite (Vondráček, A., 1904, ii, 390) are also discussed. T. H. P.

**Catalytic Actions at Solid Surfaces. V. Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1920, [1], 98, 27-40. Compare this vol. ii, 422, 423).—The curves representing the hydrogenation of methyl cinnamate, anethole, and safrole at  $140^\circ$  and  $180^\circ$  in the presence of nickel have a form for 60-80% of their length represented by  $K = v/t$ , which indicates complete hydrogenation. In the case of isoeugenol and coumarin, the hydrogenation curves show a transition from a linear to a logarithmic curve. In the case of ethyl cinnamate, instead of passing a continuous stream of hydrogen over the catalyst, the tube was closed at one end; under these conditions, the results show: (i) with increasing purity of hydrogen, the ratio,  $v/t$ , approaches the constancy characteristic of hydrogenation in a continuous stream of hydrogen; (ii) the values of  $K' = 1/t \log V'/(V' - v)$  increase throughout, but become more nearly concordant as the purity of the hydrogen decreases. As the purity of the hydrogen and the speed of the action, measured by  $v/t$ , increase, the absolute value of the constant,

$$K'' = 1/t \log V''/(V'' - v),$$

falls, that is, the rate at which the gas space becomes filled with impurity is smaller the purer the hydrogen. The hydrogenation curve of linseed oil shows an initial linear portion of about 30% of the whole curve, which corresponds with the hydrogenation of all the linolenin and most of the linolein; a very abrupt curvature then sets in, and this is followed by an approximately linear curve at a much lower slope. These experiments were carried out with 200, 300, and 400 grams of oil, and of 0.45 and 1.5 grams of

nickel. They show: (i) that the factor  $v/t$  depends on the mass of nickel present, (ii) the impurities in the oil gradually affect the catalyst, and (iii) with the smaller quantity of nickel the rates are practically the same for quantities of 200 and 300 grams of oil, but with 400 grams the linear portion of the curve is shortened, owing to the increased effect of the impurity.

It is shown that the hypothesis of unstable intermediate compounds between catalyst and reacting substances offers a reasonable explanation of the mechanism of "so-called" heterogeneous catalytic actions, and in particular for reactions of the types: (i) Action of enzymes on sugar derivatives in aqueous solution. (ii) The Sabatier catalyses of organic compounds in the presence of finely divided metals or metallic oxides, including hydrogenation and dehydrogenation, hydration and dehydration, formation of ethers and ketones, the specific action of finely divided metals on the vapours of aliphatic acids, and the combined dehydration and condensation processes effected by certain metallic oxides, leading to the production of ethers, amines, mercaptans, and esters from alcohols and phenols. (iii) The interaction of carbon monoxide and steam conditioned by various solid substances. J. F. S.

**Catalytic Activity of Copper.** I. W. G. PALMER (*Proc. Roy. Soc.*, 1920, [A], 98, 13—26).—The mechanism of the catalytic oxidation of ethyl alcohol and isopropyl alcohol by metallic copper has been studied at temperatures up to 320°. It is shown that in no circumstances, even when the copper is alloyed with zinc, does electrolytic copper exert any influence on either of these alcohols. The oxidation is effected by copper produced by the reduction of copper oxide. The reaction has been carried out in such a way that the rate is automatically registered by the liberated hydrogen. In the present case, the initial period of the reaction alone has been considered. The experimental facts are best interpreted by assuming that alcohol is selectively adsorbed by copper from a mixture of alcohol and aldehyde vapours, so that during dehydrogenation the surface of the copper is covered by a layer of alcohol molecules, and adsorption and consequent destruction of the aldehyde prevented. If it be supposed that dehydrogenation of alcohol involves three stages, (i) adsorption of alcohol molecules over the surface of the copper, (ii) activation of certain alcohol molecules by absorption of energy, and (iii) evaporation of acetaldehyde and hydrogen from the adsorption surface into the alcohol stream flowing past the catalyst, then the process bears a close physical analogy to the escape of ions from a heated solid. J. F. S.

**Conditions of Stability of Atoms.** FELIX JOACHIM DE WISNIEWSKI (*Arch. Sci. phys. nat.*, 1920, [v], 2, 301—308).—A mathematical paper in which the stability of atoms of the Bohr type is derived from the assumption that the electrical potential energy of the atom is a positive function. J. R. P.

**Constitution and Configuration of the Atom.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **94**, 513-541).—A theoretical paper in which the views recently advanced by the author on the constitution and configuration of the atoms (A., 1918, ii, 286, 304; 1919, ii, 21) are extended and modified with the object of making the hypothesis include all the elements, particularly those of the rare earths. On the basis of the present hypothesis, a spatial representation of the periodic system is developed which arranges the elements according to a cascade system, in which the steps from one plane to the next are occupied respectively by cobalt and nickel, rhodium and palladium, the metals of the rare earths, and iridium and platinum. J. F. S.

**Structure of the Atomic Nucleus.** E. GEHRCKE (*Sitzungsber. Heidelberger Akad. Wiss., Math.-naturwiss. Kl.*, [A], 1919, pp. 19; from *Chem. Zentr.*, 1920, iii, 169-170).—In continuation of the models developed previously for the lithium, glucinum, boron, and carbon atoms (this vol., ii, 241), the author now puts forward structures for the atomic nuclei of the other elements to the end of the periodic scheme. The fundamental hypothesis is that the atomic nuclei of the higher elements are merely repetitions of those of a lower horizontal series of the periodic system, with the difference that the nucleus is surrounded by a ring of  $\alpha$ -particles. Thus, for example, the atomic nucleus of sodium is identical with a lithium nucleus surrounded by a ring composed of four  $\alpha$ -particles, whilst, similarly, the potassium nucleus is identical with a sodium nucleus surrounded by a ring of four  $\alpha$ -particles. Isotopes are possible for several atoms which differ from one another by an  $\alpha$ -particle in the ring enclosing the central nucleus. The number of  $\alpha$ -particle rings is considerable in the case of the higher elements. Every element would thus appear as a compound of a primal element, H', and electron, arranged according to a systematic and not too complicated plan. Order is thus introduced into the relationship between atomic weight and atomic number, and explanations are found for a lengthy series of empirical observations, such as the chemical similarity of the rare earths, the spaces in the periodic system, etc. H. W.

**Atomic Weights and Atomic Numbers.** STEPHEN MIALl (*Chim. et Ind.*, 1920, **4**, 189-192).—If graphs are plotted of which the ordinates represent atomic weights and the abscissae the atomic numbers, that is, the positions of the elements in the periodic system, the series form nearly parallel curves. For the group of elements helium to nickel, and copper to tungsten, the curves are represented by the equation  $y = 2x + a$ , and for the group platinum to uranium by  $y = 3x + a$ . The lack of relationship between atomic weights and the properties of elements is assumed to be due to the factor  $a$ , which is known as the "inert weight"; the "active weight" of the atom determines the valency of the element, and not necessarily its chemical activity. Hydrogen does not conform

to the equation  $y = 2x + a$ ; it may be represented by  $y = x$  or  $y = \frac{1}{2}x + \frac{1}{2}$ , but probably its atom contains no inert weight.

The graphs indicate that 2.5 units of the atomic weight are normally active, whilst one unit may be chemically inactive. Assuming the atoms to consist of particles equal to 0.5 of unity, it is probable that one particle is active, and that two particles may be either active or inactive. The equation  $y = Mx + a$  represents the atomic weights of all the elements,  $x$  being the atomic number and  $a$  a small whole number, the properties of the elements being independent of  $a$ .

W. J. W.

**Periodic System of the Elements in the Light of the Theory of Radioactive Degradation.** F. KIRCHHOFF (*Zeitsch. physikal. Chem.*, 1920, **94**, 257—262).—A theoretical paper in which the position in the periodic system and the possible genesis of the elements are considered in the light of the known facts of radioactive degradation. It is shown that the atomic weights,  $A$ , of the more stable elements, which are functions of the atomic number,  $M$ , and  $I$ , the number of nucleus electrons, in that  $A = 2(M + I)$ , are periodic functions of  $I$ , since in certain parts of the periodic system  $A$  remains practically constant, and then commences to change regularly, and this reappears periodically.

J. F. S.

**Deduction of the Smoluchowski Formula of Spatial Partition of Particles in a Kinetic Field.** R. LORENZ and V. EITEL (*Zeitsch. physikal. Chem.*, 1920, **94**, 254—255. Compare A., 1914, ii, 451).—A correction of an intermediate stage in the deduction of the Smoluchowski formula previously published (*loc. cit.*).

J. F. S.

**Metastability of the Elements and Compounds as a Consequence of Enantiotropy or Monotropy.** I. ERNST JOHNSON and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 450—464. Compare A., 1916, ii, 183).—A theoretical paper in which reasons for the failure of other workers in reproducing the authors' previous work on metastable varieties of metals are enumerated. It is also pointed out that metastable varieties of elements and compounds are of much more frequent occurrence than has been generally believed. A general discussion of the conditions under which such metastable varieties may be obtained is entered into, and particular stress is laid on the influence of minute traces of impurities.

J. F. S.

**A Method for the Experimental Proof of the Molecular Theory and the Avogadro-Loschmidt Number.** A. VON SZENT-GYÖRGYI (*Zeitsch. physikal. Chem.*, 1920, **95**, 247—250).—A method is indicated by which the Avogadro number may be experimentally determined. The method consists in adding to an albumin suspension of known content various solutions of known concentration of aluminium chloride, and examining the charge

on the particles. When exactly the correct quantity of aluminium chloride has been added, so that the particles all change the cataphoresis from positive to negative, it is possible to calculate the Avogadro number on the assumption, which is substantiated, that one ion discharges one albumin particle.

J. F. S.

**Nature of the Chemical Bond; an Attempt to Find a Common Cause for the Conceptions; Auxiliary Valency and Molecular Bond.** F. HOCHERER (*Zeitsch. physikal. Chem.*, 1920, **94**, 129—148).—A theoretical paper in which an hypothesis is put forward to explain the origin of subsidiary valencies, and, at the same time, to account for the formation of double compounds, complexes, and hydrates. It is assumed, in keeping with Bohr's hypothesis, that the ordinary chemical bond is due to an oscillating electron between the two atoms concerned; this is regarded as an electric current flowing in a close circuit in which the atoms concerned lie. When two such circuits lie parallel to one another, there will naturally be an attraction set up between them, and this could well be powerful enough to hold the two compounds together, that is, a molecular compound would be formed. For such a compound to be stable, it is necessary that the bonds in the individual compounds should be parallel, and that the current in each flowing at the same rate and in the same direction, that is, the periodicity of the electron oscillation is the same in both cases. The hypothesis is illustrated in connexion with number of well-known double compounds, and it is discussed in connexion with Werner's co-ordination theory. As will be seen a new type of spatial structure is involved in this hypothesis.

J. F. S.

**Negative Valencies.** D. STRÖMHOJLM (*Zeitsch. anorg. Chem.*, 1920, **111**, 237—242).—A theoretical paper in which the valencies of negative elements are considered. It is pointed out that when a negative element forms compounds in which it acts with different valencies, these always differ by two, that is, the valencies of negative elements are always saturated in pairs. This is to be explained by assuming that in the negative elements the valency electrons are grouped together in pairs. The valency figure of  $\delta$  which dominates the negative valencies is therefore to be regarded as made up of four pairs of electrons, which constitute a completely saturated system. This is governed by the tetrahedral symmetry, and the stereochemical data show that, in the case of those elements which can enter into combination by their negative valencies, the symmetry relationships are determined by the tetrahedron.

J. F. S.

**Chemical Concepts of the Ancient Orientals.** Y. H. CHEN (*Science [China]*, 1920, **4**, 262—284).—Chemical knowledge in ancient China seems to have attained a rank comparable to that reached in Egypt. The four elements, earth, fire, air, water, formed the basis of a later chemical philosophy, which was

developed quite independently of the Occident. Theories were developed similar to those of Aristotle and of the earlier iatro-chemists. The Orient also produced a system of iatro-chemistry founded on the "Ben Tsao" written in 2838 B.C. This medical chemistry ceased its development from about 1200 A.D.

CHEMICAL ABSTRACTS.

**An. American Edition of the Elementary Treatise of Chemistry by Lavoisier, published at Philadelphia in 1799.**

GRAHAM, LUSK and JEAN LE GOFF (*Bull. Soc. chim.*, 1920, [iv], 27, 667-673).—A brief description of the various French editions of Lavoisier's work, and the subsequent English, Spanish, Italian, and Dutch translations, together with an account of an edition published in Philadelphia in 1799.

W. G.

**Improved Form of U-Tube.** E. R. DOVEY (*Analyst*, 1920, 45, 333).—The two limbs of the U-tube are brought together so that the rims at the top are in contact; the bend at the bottom of the tube is constricted, and a perforated Gooch disk is placed at the bottom of each limb.

W. P. S.

**Extraction Apparatus with Vapour Stirring.** P. WAENTIG (*Text. Forsch.*, 1920, 2, 61-62; *Chem. App.*, 1920, 7, 92-93; from *Chem. Zentr.*, 1920, iv, 265).—In order to allow the vapours of the boiling liquid to enter the extraction space, and thus to utilise their latent heat in the Soxhlet apparatus, the lower tube of the latter is sunk so deeply into the liquid in the boiling flask that its open end becomes clear of the surface of the liquid only when the extraction tube is filled almost to the level of the top of the syphon tube. To allow the vapour from the boiling liquid to pass into the syphon tube, the latter is somewhat lengthened, and terminates just above the level of the boiling liquid in the flask.

H. W.

**Air-oven Thermo-regulator.** H. M. ATKINSON (*J. Soc. Chem. Ind.*, 1920, 39, 298r).—A cylindrical float, loaded slightly with mercury and having its upper end in the form of a capillary, is contained in one limb of a U-tube filled partly with mercury. The capillary extends upwards into a tube passing through the cork closing this limb of the U-tube, the shoulder of the float and the end of the tube being ground to form a gas-tight joint when the float rises. The gas enters through a side-tube above the mercury-level, passes between the neck of the float and the tube, then into the latter and thence to the burner. The other limb of the U-tube connects with a bulb in the oven. When the float rises and cuts off the gas supply, a small quantity of gas is allowed to pass through a hole in the side of the float and escapes through the capillary to the burner, the capillary thus acting as a by-pass.

W. P. S.

### Inorganic Chemistry.

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**Preparation of Ammonia-free Water.** GERALD C. BAKER (*J. Ind. Eng. Chem.*, 1920, 12, 798—799).—Water free from ammonia may be obtained by passing distilled water through a moderately deep layer of permutite (a complex hydrated sodium aluminium silicate); a layer 30 cm. deep and 20 cm. in diameter will remove the ammonia from 450 litres of water. The activity of the permutite may be regenerated by treatment with 10% sodium chloride solution. The disadvantage of the method is that it gives a water of higher mineral content. W. P. S.

**Rate of Decomposition of Hydrogen Peroxide in the Presence of Iron Ions.** JOSEPH VON BERTALAN (*Zeitsch. physikal. Chem.*, 1920, 95, 328—348).—The rate of decomposition of hydrogen peroxide at 40° has been determined in the presence of ferrous sulphate or ferric sulphate and a little free sulphuric acid (0.01*M*). The reaction occurs in all cases as a typical unimolecular catalytic process. The velocity of reaction in acid solutions and in the presence of either ferrous or ferric ions is directly proportional to the concentration of the hydrogen peroxide and that of the iron ions, and inversely proportional to the hydrogen-ion concentration or the concentration of the free acid. The velocity of the reaction is entirely independent of the state of oxidation of the iron ions, and the catalytic action depends on the total amount of iron present, no matter what its state of oxidation. The temperature-coefficient of the reaction is 3.25 for 10°. J. F. S.

**Solubility of Halogens in the Corresponding Hydracid and Alkali Salts. II.** E. OLIVIER-MANDATA (*Gazzetta*, 1920, 50 ii, 89—98. See this vol., ii, 542). The solubilities of chlorine in sodium chloride solutions and hydrochloric acid, and that of bromine in hydrochloric and hydrobromic acids, have been measured.

The results confirm the observation that the solubility of chlorine is greater in hydrochloric acid than in water, whereas the presence of sodium chloride diminishes the solubility in water by amounts increasing with the proportion of salt present. The coefficient of solubility of the chlorine diminishes as the concentration of sodium chloride increases, but the expression  $(\alpha' - \alpha)/M$  gives constant values,  $\alpha'$  and  $\alpha$  representing the coefficient of absorption of chlorine in water and sodium chloride solution respectively, and  $M$  the concentration of the salt in gram-mols. per litre of solvent. This empirical formula has been verified (Gordon, A., 1896, ii, 154) for the solubility of indifferent gases in aqueous solutions of electrolytes, so that chlorine behaves differently from the other halogens, which exhibit almost the same solubility in solutions of the corresponding hydracids and in those of the alkali salts. T. H. P.

**Action of Light on Moist Chlorine.** ERNST RADEL (*Zeitsch. physikal. Chem.*, 1920, **95**, 378—383).—Using the ultra-microscopic method, the reaction between chlorine and hydrogen has been studied. It is found that when moist chlorine is illuminated an induction period is set up which varies between 1/100 sec. and 30 secs., after which a fine fog is produced which rapidly forms drops. On removing the light the particles become smaller, and eventually disappear. The same effect is observed when the chlorine is ionised by a spark from an induction coil or by the light from a Tesla transformer. Radiation from polonium or radium bromide has the same effect, but much weaker. J. F. S.

**Concentration of the Lighter Isotopes of Iodine.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1920, **95**, 95—125).—In an earlier paper (this vol., ii, 610) the author has shown that in all probability five isotopes of iodine exist which have atomic weight 122, 124, 126, 128, 130, depending on their origin. This involves differences varying between -3.88% and +2.43% from the mean value, 126.92, of the atomic weight. Vapour density determinations have been carried out by the Dumas method with iodine which has been twice sublimed, thrice sublimed, recrystallised from carbon disulphide, separated by diffusion, and fractionated. Ten experiments with twice sublimed iodine give an atomic weight which has a mean divergence of 2.04% from the accepted value; eight experiments with fractionated iodine give a mean divergence of 1.33%. Of twenty-seven experiments, not one gives atomic weights which are equal to or less than the accepted value. The lowest value obtained for the atomic weight is 128.22. An apparatus is described by means of which a possible separation of the isotopes may be brought about by diffusion. J. F. S.

**Preparation of Iodic Acid and its Anhydride.** ARTHUR B. LAMB, WILLIAM C. BRAY, and WALTER J. GELDARD (*J. Amer. Chem. Soc.*, 1920, **42**, 1636—1648).—A simple and rapid method has been developed for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24—26% chloric acid solution, the evaporation of the solution and the dehydration of the iodic acid. The product is pure white, has practically 100% of the oxidising value, and contains no detectable impurities except traces of water and barium iodate. It is decidedly more stable towards heat than iodic anhydride as ordinarily prepared, and, therefore, has decided advantages for use in the analysis of small quantities of carbon monoxide in air. The yield of pentoxide is almost theoretical. In the preparation a small excess (3%) of chloric acid is used; this ensures the complete removal of the hydrochloric acid formed during the oxidation process, which otherwise would reduce the iodic acid during evaporation. When this small excess of chloric acid is used, the net result of the oxidation is expressed by the equation  $I_2 + 2HClO_4 = 2HIO_3 + Cl_2$ . The mechanism of this reaction undoubtedly does not correspond with



a direct replacement of chlorine by iodine. The chloric acid solution is made by the direct action of sulphuric acid on barium chlorate solution. There is no decomposition of the chloric acid, and the only loss is the small amount of solution absorbed by the barium sulphate. This method of preparation presents no difficulties on the manufacturing scale.

J. F. S.

**Colloidal Sulphur.** PAUL BARY (*Compt. rend.*, 1920, 171, 433—435).—Colloidal sulphur in the form of a limpid liquid is a hydrophile colloid, capable of absorbing water. This absorption is favoured by the presence in solution of small amounts of salts of univalent metals, whilst it is prevented by the action of salts of bivalent metals. Such colloidal sulphur is not pure sulphur, but a compound containing sulphur in a highly polymerised state. The compounds are easily dissociable, and only exist in aqueous medium in the presence of substances which limit their decomposition. When the swelling of the granules, due to the absorption of water, becomes small, the granules lose their transparency and the liquid becomes milky and loses its stability.

W. G.

**Freezing Points of Mixtures of Sulphuric and Nitric Acids.** W. C. HOLMES (*J. Ind. Eng. Chem.*, 1920, 12, 781—783).

—The freezing points of mixtures of sulphuric and nitric acids containing 0 to 50% of the latter were determined in test-tubes immersed in an insulated bath of ether and carbon dioxide snow, and the results plotted as curves. In the case of mixtures with a total acidity of 100% the freezing point reached a minimum ( $-18.2^{\circ}$ ) when 5.4% of nitric acid was present, and a maximum ( $+2.3^{\circ}$ ) with 10.8% of nitric acid. The curve closely resembled that of sulphuric acid and water, which reached a minimum ( $-34^{\circ}$ ) with 8.4% of water, and a maximum ( $+8^{\circ}$ ) with 15.5% of water. It is probable that at the maximum point in the nitric acid mixtures a definite compound,  $5\text{H}_2\text{SO}_4\cdot\text{HNO}_3$ , is present, whilst the minimum point coincides with a compound of the approximate composition  $5\text{H}_2\text{SO}_4\cdot 4\text{HNO}_3$ . In the determinations with mixtures of a total acidity of 95% the freezing point fell to  $-41.0^{\circ}$  with 2.35% of nitric acid, then rose to  $-11.0^{\circ}$  with 9.75%, and fell again to  $-41.3^{\circ}$  with 49.09%. With mixtures of a total acidity of 103% the minimum ( $-12.3^{\circ}$ ) was reached with 8.15% of nitric acid and the maximum ( $+10.5^{\circ}$ ) with 15.52%. The last two series of results were complicated by the presence of water and sulphur trioxide respectively.

C. A. M.

**Vapour-pressure Curves of Solid and Liquid Selenium near the Melting Point.** L. E. DODD (*J. Amer. Chem. Soc.*, 1920, 42, 1579—1594).—The sublimation curve for crystalline selenium (hexagonal) has been determined over the temperature range  $190-215^{\circ}$  by the method of molecular flow. By the same method data for the vaporisation curve for the liquid of vitreous amorphous selenium have been obtained over the temperature range

220—235°. The relation between vapour pressure and temperature for selenium over the temperature range considered and on the basis of a diatomic vapour may be expressed by a simple exponential equation,  $p = c_1 \cdot e^{\alpha/T}$ , where  $T$  is the absolute temperature. On the basis of a diatomic vapour the results appear to locate the melting point at 217.4°, and give a pressure value at the melting point of 12.68 bars (0.00954 mm.), and slope values for the  $p$  and  $T$  curves at the melting point of 1.350 bars/degree (0.000767 mm./degree) for the crystals, and 0.573 bar/degree (0.000431 mm./degree) for the liquid. The slope at the melting point was thus found to be greater for the solid than for the liquid, as required by thermodynamics, and as found for other substances. The difference between the two slopes is 0.477 bar/degree (0.000358 mm./degree) on the basis of a diatomic molecule. From Clapeyron's first latent heat equation, the three latent heats at the melting point were calculated on the basis of a diatomic vapour, as follows: latent heat of vaporisation, 135.5; latent heat of sublimation, 219.4; and latent heat of fusion, 83.9 cal./gram. Since the vapour density at the experimental temperatures is unknown, the three latent heats, as well as the pressure at the melting point, and the slopes of the  $p$  and  $T$  curves at the melting point, have been calculated on the basis of 4, 6, 8, 10, and 12 atoms per molecule of vapour. The calculated latent heat values vary inversely as these numbers. These results are not out of keeping with the requirements of the Kirchhoff equation, based on thermodynamics, relating vapour pressure and temperature, but they do not give positive evidence that this equation is applicable to selenium, as would be expected from the limited temperature range even if that relation should apply. J. F. S.

**Tellurium Nitrite.** FELIX VON OEFLE (*Pharm. Zentr.-h.*, 1920, 61, 491—492).—By the action of nitric acid on tellurium, under certain conditions, namely, using large quantities of material and a high column of liquid (not less than 50 cm.), tellurium nitrite was obtained as a flesh-coloured precipitate, which could be dried at 100° without decomposition. At higher temperatures it decomposes, leaving a residue of yellow tellurium dioxide. E. H. R.

**Rutherford's Experiments on the Subdivision of the Nitrogen Nucleus.** W. LENZ (*Naturwiss.*, 1920, 8, 393; from *Chem. Zentr.*, 1920, iii, 300).—The priority in the explanation of the deficit in the atomic weight by the theory of the lag of energy should be ascribed to Swinne, and not, as previously (this vol., ii, 427), to Harkins and Wilson. H. W.

**Determination of the Electrolytic Potential and Over-voltage of Arsenic.** VINCENT B. MARQUIS (*J. Amer. Chem. Soc.*, 1920, 42, 1569—1573).—The normal potential of an arsenic electrode has been calculated from *E.M.F.* measurements of cells of the type  $\text{Hg}, \text{HgCl} | \text{LiCl} \text{ in absolute alcohol} | \text{AsCl}_3$  (0.176*M*) in

absolute alcohol|As. This cell had an *E.M.F.* of 0.153 volt, which, making use of the Rideal and Roderburg method of calculation, is equivalent to 0.040 volt for the arsenic-alcohol potential and 0.111 volt for the arsenic-water potential. From this, the electrode potential, 0.138 volt, is obtained, which places arsenic between hydrogen and copper in the electrode series. The molecular conductivity of arsenic trichloride in alcohol has been determined at 20°, and concentration-conductivity curves drawn. The dissociation of arsenic trichloride in alcohol solution is 20.6% in 0.176*M*-solution. Conductivity determinations also show that there is no appreciable hydrolysis of arsenic trichloride in alcohol solution, but that there is a slight combination with the solvent. The hydrogen overvoltage on arsenic electrodes has been determined by both the open-circuit and closed-circuit methods. The former method gives a value 0.379 volt and the latter 0.478 volt.

J. F. S.

**A Decolorising Carbon.** JOSEPH C. BOCK (*J. Amer. Chem. Soc.*, 1920, **42**, 1564--1569).—The decolorising action of a vegetable carbon, sold under the name Norit, on biological fluids has been investigated. Norit is found to extract uric acid completely from urine; creatinine is extracted to a large extent, carbamide, total nitrogen and phosphates are removed to a considerable extent, and ammonia nitrogen, chlorides and dextrose are slightly removed. Bouillon cultures, on shaking with norit for a few seconds and subsequently keeping in contact for three to four minutes, showed a marked decrease in the number of bacteria. Freundlich's simple adsorption formula holds exactly for the adsorption of total nitrogen and creatinine, and probably holds for dextrose. When several substances are present in a given solution, each one of them is adsorbed less than when they are present separately. Thus urine containing 1.77% of dextrose loses no sugar on treatment with norit, whereas a 0.77% aqueous solution of dextrose loses 16.8% of its sugar after the same treatment. Lactose is removed from milk by norit. Washed norit (ash, 2.18%) is more efficient than commercial norit (ash, 5.13%) as an adsorbent.

J. F. S.

**The Strength of Aqueous Carbonic Acid Solutions at High Pressures.** OTTO HANSEL (*Centr. Min.*, 1920, 25—32).—Experiments were made to determine the solubility of carbon dioxide in water at higher pressures, and the electrical conductivity of the solutions. The solutions were prepared by saturating water with carbon dioxide in an autoclave of large capacity. When the pressure had been measured, a quantity of the saturated solution was removed to a special coulometer, and the excess of gas allowed to escape from the solution at atmospheric pressure, the volume of gas and water being then measured. Determinations were made at 0° at pressures up to 38 atm. and at 15° up to 52 atm. At 0° and 38 atm., a saturated solution contains 7.44% by weight of carbon dioxide, and at 15° and 52 atm., 5.44%. Henry's law

is not obeyed, for the rate of increase in solubility diminishes with increasing pressure. The electrical conductivity of the solutions is very low; thus, a 2.99% solution, at 15° and 20 atm., has a conductivity only half that of a 0.3% solution of acetic acid. It has been shown, however, by Thiel and Strohecker (A., 1914, ii, 361) that in a 0.038% solution of carbon dioxide at 4°, only 0.56% exists in the hydrated form, as  $\text{H}_2\text{CO}_3$ . If the same holds true at higher concentrations and pressures, the true concentration of carbonic acid in a saturated solution at, say, 15° and 52 atm., is 0.027%, and its conductivity,  $1.98 \times 10^{-4}$ , is of the same order as that of formic acid at a similar concentration. Carbon dioxide must, then, be classed with the stronger acids, a conclusion which accords fully with the known activity of the acid in rock formation and degradation.

E. H. R.

#### Preparation of Thiocarbonyl Tetrachloride.

PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1920, **39**, 256–257r).—For the preparation of thiocarbonyl tetrachloride on a large scale, 4 grams of iodine are added to 2 kilos. of carbon disulphide dried over calcium chloride, dry chlorine is passed in, the temperature not being allowed to exceed 20°, until the increase in weight corresponds with the absorption of five atomic proportions of chlorine, when the reaction mixture is run, in a thin stream, into hot water through which steam is being blown. Sulphur chloride is thus decomposed, and thiocarbonyl tetrachloride distils over. The latter is again distilled with steam, then dried over calcium chloride, and fractionally distilled until the temperature reaches 140°. The residue in the flask is the required thiocarbonyl tetrachloride, and by this process a 60% yield may be obtained. It should be noted that thiocarbonyl tetrachloride is completely decomposed by contact with metallic iron at the ordinary temperature. W. G.

#### Behaviour of Concentrated Alkali Chloride Solutions in Presence of Alkali Hydroxides.

CH. CHOROWER (*Zeitsch. angew. Chem.*, 1920, **33**, 201–203).—The author has investigated the solubility of alkali chlorides in liquors derived from the treatment of vinasses ash with lime and barium hydroxide. The composition of an experimental liquor was: Cl, 3.559; OH, 0.9278; K, 4.792; Na, 0.933; S, 0.0594;  $\text{SO}_4$ , 0.0321;  $\text{CO}_3$ , 0.0705%. The liquor was evaporated in quantities of 4 litres, and boiling-point determinations were made at various stages when deposition of salts ceased. The density was then determined in a modified pycnometer, and the samples analysed. Six samples tested from quantities of 15, 20, 25, 35, 41, and 48 litres, with boiling points 110°, 111°, 112°, 115°, 116°, and 118°, showed increasing densities from 1.295 to 1.370. The chlorine ions diminished from 12.58 to 7.661, and potassium ions remained nearly constant at approximately 17, but all the other ions gave progressively rising values. The author discusses the phenomena by the application of the theory of mass action and of the phase rule.

W. J. W.

**Oxidation of Potassium Plumbite to Plumbate by means of an Alternating Current.** FRANZ JIRSA (*Zeitsch. physikal. Chem.*, 1920, **94**, 1—5).—The electrolysis of a solution (*N*) of potassium hydroxide between lead electrodes by means of an alternating current of 49 periods brings about the formation of potassium plumbite as the only product. It is shown that the plumbite may be electrolytically oxidised to plumbate if electrodes of suitable metals are used. The metals copper, silver, gold, cadmium, magnesium, mercury, nickel, iron, platinum, and palladium when used as electrodes with alternating current effect the oxidation but no oxidation occurs when lead, bismuth, cobalt, thallium, or carbon is used. The nature of the electrode is also determinative of the product of the oxidation; under the same conditions (40 grams of potassium hydroxide and 4.5 grams of lead oxide per litre) with palladium electrodes, yellow lead sesquioxide separates and lead metaplumbate is formed, whilst with nickel or iron electrodes a dark brown powder separates, which is the dioxide, and the yellow plumbate is not formed. It is shown also that, even with electrodes which are capable of effecting oxidation, oxidation does not always take place; under certain conditions, reduction, or even oxidation and reduction, may occur. The disintegration of the electrodes is an accelerating factor of the reaction. J. F. S.

**Sodium Phosphide.** E. TOMKINSON and G. BARKER (*Chem. News*, 1920, **121**, 104—105, 177).—When sodium is heated with red phosphorus, amongst other products, a grey mass is obtained, which is acted on violently by water, giving spontaneously inflammable hydrogen phosphide. With yellow phosphorus under suitable conditions, a white, crystalline product is obtained. W. G.

**The Third and the Fourth Dissociation Constants of Pyrophosphoric Acid and the Examination of the Purity of Sodium Pyrophosphate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 474—481). The hydrogen-ion concentration of dilute solutions of sodium pyrophosphate was determined colorimetrically by comparing the colour change of thymolphthalein in these solutions and in mixtures of carbonate and hydrogen carbonate solutions of known  $p_H$  value. From the results, a mean value of  $4.6 \times 10^{-9}$  for the fourth dissociation constant was calculated. Further measurements with mixtures of pyrophosphate and small quantities of hydrochloric acid, so as to give the ion  $\text{H}_2\text{P}_2\text{O}_7^{4-}$  in presence of  $\text{P}_2\text{O}_7^{4-}$ , led to the result  $K_4 = 3.6 \times 10^{-9}$ , with certain assumptions as to the degree of dissociation of the solution. The third dissociation constant was determined in a similar way by measurements in mixed solutions of  $\text{Na}_4\text{H}_2\text{P}_2\text{O}_7$  and  $\text{Na}_6\text{P}_2\text{O}_7$ ; the value  $K_3 = 7.6 \times 10^{-7}$  being obtained. W. S. M.

**Metastability of the Metals as a Consequence of Allotropy and its Significance for Chemistry, Physics, and Technics.**

**IV. ERNST CONEN and H. B. BRUNS** (*Zeitsch. physikal. Chem.*, 1920, **94**, 443—449. Compare *A.*, 1914, ii, 52, 202, 332, 652, 793; 1915, ii, 52, 83, 417, 471, 565, 634; 1916, ii, 183).—A repelition

of earlier experiments in which a change in density of silver and cadmium was found after keeping under solutions. This change has been attributed to the adsorption of water or solution. The present experiments were undertaken to ascertain whether or no the metal does contain water after the treatment. The results show that whilst water is contained in the metals to the extent of 0.1—0.001%, the amount is so small as to be without effect on the density, and consequently can play no part in the changes previously observed.  
J. F. S.

**Binary System Äkermanite-Gehlenite.** J. B. FERGUSON and A. F. BUDDINGTON (*Amer. J. Sci.*, 1920, [iv], 50, 131—140. Compare Ferguson and Merwin, A., 1919, ii, 459).—The binary system äkermanite ( $2\text{CaO}, \text{MgO}, 2\text{SiO}_2$ )-gehlenite ( $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ ) has been studied by the quenching method, and the curves of the solid and the liquid phases constructed. The system is found to consist of a complete series of solid solutions with a minimum melting point,  $1388^\circ$ ,  $70^\circ$  below that of äkermanite ( $1458^\circ$ ). The refractive index and general optical characteristics have been determined for the intermediate compositions, and are found to be a continuous function of the composition. Crystals of a certain intermediate mixture are isotropic for sodium light, and constitute a transition phase from crystals of positive optical character to those of negative optical character. Zoned crystals showing material of both positive and negative optical character in the same crystal were obtained. These are analogous, in this respect, to certain natural melilite crystals which have been previously described. The densities of crystals of äkermanite, gehlenite, and several intermediate mixtures have been determined and found to confirm the isomorphous character of the system. Äkermanite was found to show the unusual feature of its glass having a greater density (2.955) than the corresponding crystals (2.944) at  $25^\circ$ .  
J. F. S.

**Piezo-chemical Studies. XVI. Experimental Proof of Braun's Law by an Electrical Method.** ERNST COHEN, C. W. G. HETTERSCHIJ, and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, 94, 210—232. Compare A., 1919, ii, 321).—Braun's law has been experimentally examined for the case of cadmium iodide by the electrical method of Cohen and Sinnige (A., 1909, ii, 981), and it is shown that within the limits of the experimental error this law accurately represents the experimentally found facts. To arrive at this conclusion the following data have been obtained for cadmium iodide: temperature-coefficient of the solubility,  $(\partial x/\partial T)_{30^\circ} = +0.1003 \pm 0.001$  gram per 100-gram solution/degree; pressure-coefficient of the solubility,  $(\partial x/\partial \pi)_{30^\circ} = -0.00390 \pm 0.0002\%$ /atm.; the fictitious volume change,  $\Delta V' = 0.0191 \pm 0.0003$  c.c./gram, and the fictitious heat of solution,  $Q_{30^\circ} = 3.71 \pm 0.07$  gram-cal./gram. Substituting the first three of the above quantities in Braun's equation, the value of  $Q$  is found to be  $3.60 \pm 0.19$  gram-cal./gram. The determination of the pressure-coefficient of the solu-

bility indicates that this factor may no longer be regarded as negligibly small.

J. F. S.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. III. Cadmium Iodide.** ERNST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1920, **94**, 471—481. Compare this vol., ii, 620).—Cadmium iodide has been carefully examined, and it is shown that at temperatures between that of the melting point and ordinary temperature, it exists in two modifications which stand to one another in monotropic relations. Cadmium iodide obtained by crystallisation from solution or by sublimation is a mixture of  $\alpha$ - and  $\beta$ -forms in unknown quantities. The physical properties of cadmium iodide hitherto recorded, except those recorded by Cohen, Hetterschij, and Moesveld (preceding abstract), refer to a mixture of the  $\alpha$ - and  $\beta$ -forms of unknown composition.

J. F. S.

**Melting Points and Thermoelectric Behaviour of Lead Isotopes.** THEODORE W. RICHARDS and NORRIS F. HALL (*J. Amer. Chem. Soc.*, 1920, **42**, 1550—1556).—The melting points of two isotopic varieties of lead, which differed by 0.8 in atomic weight, have been determined and found to differ by not more than 0.05°. From this result it may be assumed that the other kinds of lead not only have very nearly the same melting point, but also, since the sample consisting chiefly of lighter isotopes doubtless contained ordinary lead, that they mix or, better, mutually dissolve without affecting the melting point. The Seebeck thermoelectric effect produced at the junction of the two kinds of lead was determined and found to be zero. (See also A., 1916, ii, 250.)

J. F. S.

**Disglomeration: a New Mode of Transformation of Solidified Metals.** A. THIEL (*Sitzungsber. Ges. gesamt. Naturwiss. Marburg*, 1920, i, 1—17; from *Chem. Zentr.*, 1920, iii, 227).—The allotropy of lead does not play any part in the transformation of lead according to Heller's experiments (A., 1915, ii, 634; compare also Cohen and Heldermaun, A., 1915, ii, 456). Disglomeration (disintegration in consequence of the solution of the eutectic formed by lead and its impurities and located between the lead crystals) is a consequence of the chemical action of the dissolved nitrate and formation of lead nitrite. Disglomeration only occurs with solidified metals (copper in addition to lead). Formation of the lead tree is only observed when local, short-circuited, ionic concentration cells are developed. All types of lead which separate as the lead tree are crystallographically identical with that which has crystallised from the molten metal; the earlier explanation of the phenomenon as being due to allotropy is therefore excluded.

H. W.

**Rate of Dissolution of Metallic Copper in Aqueous Ammonia.** EIICHI YAMASAKI (*Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 169—220).—The copper was vigorously rotated with a con-

stant velocity in ammonium hydroxide, and a steady current of air passed through. Two chemical actions take place in the solution, the electrolytic dissociation of the copper and the autocatalytic reaction of cuprammonium compound in solution. The velocity of the former increases proportionally to the square root of concentration of free oxygen, and the rate of the latter to that of the cuprammonium compound. The total velocity is independent of the concentration of free ammonia and the nature of the anions. The dissolution velocity increases regularly to a maximum and then decreases again. The maximum is attained at a concentration of cuprammonium hydroxide, which is practically proportional to the concentration of free ammonia. The range of solution of copper is increased by the presence of an ammonium salt. A mathematical formula is obtained which represents the course of the reaction with sufficient accuracy. The velocity of dissolution is found to be roughly proportional to a two-thirds power of the rate of stirring. The temperature-coefficient is only 1.15, so that probably the velocity of reaction is chiefly determined by that of diffusion. Diffused daylight has no effect on the velocity. With the addition of hydroxylamine, dissolution takes place very slowly, probably due to the checking of the autocatalytic action of the dissolved copper. Sodium oleate has a retarding effect, and amalgamation considerably reduces the velocity. The effect of carbon monoxide is slight, but hydrogen peroxide increases the initial velocity of dissolution. The best conditions for the preparation of the solution of cuprammonium hydroxide are discussed on the basis of the present investigation in view of its importance in the manufacture of artificial silk.

T. H. B.

**Similarity in Micrographic Appearance Existing at Different States between Iron-Carbon Alloys (Steels), Copper-Tin Alloys (Bronzes with Tin), Copper-Zinc Alloys (Brasses), and Copper-Aluminium Alloys (Bronzes with Aluminium).** A. PORTEVIN (*Compt. rend.*, 1920, 171, 350—353).

—In the case of copper-tin and copper-aluminium alloys the austenitic, martensitic, and troostitic states have previously been observed, as well as the two aspects of the eutectoid. For copper-zinc alloys the austenitic and troostitic states have been observed, and the author has now obtained microphotographs showing first the eutectoid resolved during cooling, and secondly the martensitic state for these alloys.

W. G.

**Chemical and Electrochemical Properties of Copper-Zinc Alloys Prepared by Melting or by Electrochemical Processes.** FRANZ SAUERWALD (*Zeitsch. anorg. Chem.*, 1920, 111, 243—279).

—An account is given of the action of various reagents, such as solutions of cadmium sulphate, copper sulphate, sulphuric acid, hydrochloric acid, thallous sulphate, lead chloride, lead nitrate, and alkali sulphides, on alloys of zinc and copper prepared by various methods and of varying composition. The *E.M.F.* of alloys (100—18.4% Cu) against a solution of zinc chloride has also been measured, and the change with temperature ascertained. It is



shown that the behaviour of zinc-copper alloys is governed by the two factors which determine the chemical and electrochemical behaviour of mixed crystals, namely, the nature of the partition of the components and the mobility of the atoms in the crystal lattice. It is shown that the mixed crystals, obtained by melting, with ordered partition corresponding with the equilibrium conditions, have chemical and electrochemical properties at the ordinary temperature which to a large extent are independent of the concentration. This is to be attributed to the protecting action of the copper. The properties change sharply and suddenly only on the appearance of a new crystal form with a different lattice, whereby in the case of copper saturated with  $\gamma$ -crystals, the properties of the compound  $\text{Cu}_2\text{Zn}_3$  were observed. At  $380^\circ$ , where a considerable mobility of the atoms in the lattice exists, the electrochemical properties of the mixed crystals are dependent on the concentration, since the copper is no longer able to afford a protecting action. In the case of unordered atom partition, which is obtained by electrolytic deposition at the ordinary temperatures, the copper is only able to afford a very slight protecting action to the zinc. From this the simple relationship follows that the logarithm of the solution pressure of the zinc in alloys with unordered partition is proportional to the number of unprotected zinc atoms. The atom partition brought about by electrolysis is to a large extent dependent on the temperature, for it is shown that by the electrolysis of molten salts at  $300^\circ$  an alloy is obtained in which the atom partition is very nearly that of the equilibrium condition. J. F. S.

**Topochemical Reactions. Formation and Behaviour of Copper Hydroxide.** V. KOHLSCHÜTTER and J. L. TÄSCHER (*Zeitsch. anorg. Chem.*, 1920, **111**, 193—236).—A topochemical reaction is defined as one which depends on the relative position in space of the reacting groups or molecules. The present paper gives a long account of the various methods of preparation of copper hydroxide and the properties of the various products. In particular the loss of water from the hydroxide to form oxide and partly dehydrated hydroxides is considered. Four means of dehydrating copper hydroxide are considered: (i) thermal separation of water,  $\text{Cu}(\text{OH})_2 \rightarrow \text{CuO} + \text{H}_2\text{O}$ ; (ii) separation of water by osmotic pressure owing to the evaporation of the surrounding liquid; (iii) endosmotic drying of the hydrated compound on an anode; and (iv) water separation by internal neutralisation, due to amphoteric ionisation. The authors are of the opinion that the dehydration of copper hydroxide takes place according to the last-named method. The process is represented by the equations  $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{Cu}^{++} + 2\text{OH}^-$ ;  $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{CuO}_2^{2-} + 2\text{H}^+$ ;  $\text{HO} \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$ ; and  $\text{CuO}_2^{2-} + \text{Cu}^{++} = 2\text{CuO}$ . J. F. S.

**The Electro-affinity of Aluminium. III. The Acidity and Constitution of Aluminic Acid.** JAROSLAV HEYROVSKÝ (*T.*, 1920, **117**, 1013—1025).

**Hydrates of Aluminium Nitrate.** KENZO INAMURA (*J. Tokyo Chem. Soc.*, 1920, **41**, 1-8).—Mixtures of aluminium nitrate ( $18\text{H}_2\text{O}$ ), nitric acid, and water in various proportions are left for one to two days at  $25^\circ$ . After the equilibrium is established, the solution is separated from the residue, and aluminium, nitric acid, and water are estimated in the two fractions. The results are given in two tables and two curves, which show that in proper concentrations of nitric acid, at  $25^\circ$ , the nitrate produces three hydrates containing 18, 16, and 12  $\text{H}_2\text{O}$  respectively. The first hydrate is most stable in 73% ( $D^{15}$  1.435) or a weaker nitric acid, the next hydrate in 73-81% ( $D^{15}$  1.435-1.463), and the last in nitric acid stronger than 81%. CHEMICAL ABSTRACTS.

**Phosphomolybdic and Phosphotungstic Acids and Allied Substances.** HSEIN WU (*J. Biol. Chem.*, 1920, **43**, 189-220).—The somewhat confused literature on these acids is reviewed. There are two series of these complex acids, in which the ratios  $\text{P}_2\text{O}_5:\text{XO}_3$  are 1:18 and 1:24 respectively, and simple methods for their preparation are given.

There appear to be two isomeric forms of the phosphotungstic acid,  $\text{P}_2\text{O}_5.18\text{WO}_3$ , and there are a number of complex acids containing both molybdenum and tungsten which belong to both the 18- and the 24-series.

On moderate reduction, the complex acids give rise to a number of new complex acids containing lower oxides of molybdenum and tungsten. The value of the complex acids of phosphorus and tungsten or molybdenum as analytical reagents is fully treated.

J. C. D.

**An Approximate Determination of the Melting-point Diagram of the System Zirconia-Silica.** E. W. WASHBURN and E. E. LIBMAN (*J. Amer. Ceram. Soc.*, 1920, **3**, 634-640).—The melting points of mixtures of zirconia and silica were determined by heating one end of a small rod, 5 cm. long and 0.3 cm. in diameter, in an oxy-acetylene flame and measuring the temperature of the droplets of fused material with an optical pyrometer. Temperature readings could be duplicated to about  $\pm 100^\circ$ . By this means, it was found that the melting point of pure zirconia is about  $2700^\circ$ , and that of natural zircon about  $2300^\circ$ . A eutectic between  $\text{ZrO}_2$  and  $\text{ZrSiO}_4$  occurs near  $2300^\circ$ . [See *J. Soc. Chem. Ind.*, 628A.] A. B. S.

**Metastability of Elements and Compounds as a Consequence of Enantiotropy or Monotropy. II. Antimony Tri-iodide.** ERNET COHEN and H. R. BRUNS (*Zeitsch. physikal. Chem.*, 1920, **94**, 465-470. Compare this vol., ii, 620).—Antimony iodide has been stated by Cooke (*Proc. Amer. Acad.*, 1878, **5**, 1, 72) to belong to the enantiomorphic substances, and to crystallise in red, hexagonal crystals and yellow, rhombic crystals with a transition point at  $114^\circ$ . This change has been carefully

re-examined, and it is shown that antimony iodide is a monotropic substance, and that the temperature  $114^{\circ}$  found by Cooke was accidental. Antimony iodide prepared by sublimation is a meta-stable system, which may remain unchanged for long periods even at low temperatures.

J. F. S.

### Mineralogical Chemistry.

**Regular Grouping of Two Minerals in Titaniferous Iron-ores.** A. LACROIX (*Compt. rend.*, 1920, 171, 481—485).—The compound  $\text{FeTiO}_3$  (corresponding with  $\text{TiO}_2$  52.65,  $\text{FeO}$  47.35%) is represented most nearly in nature by the mineral crichtonite from Oisans, Isère, and it is proposed to limit this name to such a compound. In most ilmenites, however, the composition is more complex, and was represented by Rammelsberg as  $\text{FeTiO}_3 + x\text{Fe}_2\text{O}_3$ . These two components have been assumed to form an isomorphous mixture (although they do not possess the same degree of symmetry) or to form a solid solution; or, again, the isomorphous mixing of  $\text{Ti}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  has been assumed. Specimens of ilmenite from Madagascar, however, show very distinctly a fine, lamellar intergrowth of two minerals (crichtonite and hæmatite) similar to the perthitic intergrowth of the felspars. The layers of hæmatite are attacked by hydrochloric acid, leaving, finally, isolated lamellæ of crichtonite. Analysis by Raoult of a specimen from Andongovato, near Itrongay, gave:

$\text{TiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	Total	Sp. gr.
27.41	23.99	0.22	0.25	47.95	99.82	4.96

corresponding with hæmatite 47.95 and crichtonite 51.87%. The original ilmenite from the Ilmen Mts. (containing  $\text{TiO}_2$  45—48%) appears to be homogeneous, but the washingtonite variety from Litchfield, Maine ( $\text{TiO}_2$  22—24%), shows very distinctly the perthitic intergrowth, whilst in crystals from Snarum, Norway ( $\text{TiO}_2$  6—10%), the bands of crichtonite are very thin. The name ilmenite is therefore reserved for the homogeneous types, and washingtonite for those showing the intimate intergrowth of the two minerals. Similar regular intergrowths are also shown by the titaniferous magnetites of Madagascar, the two minerals in this case being magnetite and crichtonite. Layers of needles of brown rutile enclosed parallel to the octahedral planes of the magnetite are shown to be due to the secondary transformation of crichtonite.

L. J. S.

**Blödite and other Minerals of the Saliferous Stratum of Monte Sambuco in the Calascibetta Region (Sicily).** P. MILLOSEVICH (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 344—347).—Crystals of blödite, some colourless and others red, owing to

inclusions of ferric oxide, occur locally in the deposit of hard salt, consisting essentially of kieserite and rock-salt, found in the saliferous mass of Monte Sambuco; they belong to the monoclinic system,  $a:b:c=1.34939:1.067047$ ,  $\beta=79^{\circ}21'42''$ . The percentage composition:

Na <sub>2</sub> O.	MgO.	SO <sub>4</sub> .	H <sub>2</sub> O.	Insol.	Total.
18.51	12.00	47.41	21.42	0.49	99.83

agrees well with the formula  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ .

The name blöditte has a prior claim to astracanite, which was used first to indicate the rock, that is, the material forming distinct layers in the saliferous deposits, such as those of the salt lakes of the Astracan steppe.

The astracanite mass of the upper gallery of Monte Sambuco contains many rounded, white nodules, which vary in size (peas to oranges), have a granular, saccharoid structure, deliquesce partly in moist air, contain boric acid, magnesium, and chlorine, and closely resemble the nodules of compact boracite (stassfurtite) occurring among the carnallite of the Stassfurt deposits.

T. H. P.

**Optical Properties of Anthophyllite.** N. L. BOWEN (*J. Washington Acad. Sci.*, 1920, 10, 411—414).—A revision of the optical constants for Penfield's (1890) original material from Franklin, North Carolina (containing  $\text{SiO}_2$  57.98,  $\text{Al}_2\text{O}_3$  0.63,  $\text{FeO} + \text{MnO}$  10.70,  $\text{MgO}$  28.69%). gave:  $\alpha=1.6195$ ,  $\beta=1.6301$ ,  $\gamma=1.6404$ ,  $\gamma-\alpha=0.0209$ ,  $2V=88^{\circ}46'$  (Na). For the artificial magnesium metasilicate (kupfferite) described by Allen, Wright, and Clement (1906), revised values are:  $\alpha=1.584$ ,  $\gamma=1.597$ . In anthophyllite, the refractive indices increase regularly with the percentage of ferrous oxide.

L. J. S.

**The Existence in Madagascar of a Silicate of Scandium and Yttrium, Thortveitite.** A. LACROIX (*Compt. rend.*, 1920, 171, 421—423).—Thortveitite has been found in the pegmatite at Befanamo, in Madagascar, and resembles in its properties the same mineral previously discovered in Iveland, Norway, and described by Schetelig (*A.*, 1912, ii. 56).

W. G.

## Analytical Chemistry.

**Theory of Indicators Used in Acidimetry.** GUSTAV F. HÜTTIG (*Zeitsch. physikal. Chem.*, 1920, 95, 280—284).—A theoretical paper in which the results of Wegscheider (*A.*, 1916, ii, 108) and the previous paper of the author (*A.*, 1914, ii, 597) are discussed, and the optical and electrochemical behaviour of indicators further developed.

J. F. S.

**A Polychromatic Indicator.** JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 6—8).—The indicator is 3:3-dihydroxybenzaurine-2-sulphonic acid, and is prepared by condensing catechol with *o*-sulphobenzoic acid. It exhibits the following range of colours in acid and alkaline solutions: strong acid, purplish-pink; dilute acid ( $N/10$ ), salmon-orange; more dilute acid ( $N/40$ ), yellow; neutral solution (or, more exactly,  $p_H=6.5$ ), practically colourless; dilute alkali ( $p_H=7.5$ ), violet; stronger alkali ( $p_H=10$ ), indigo-blue; concentrated alkali, grass-green.

W. P. S.

**Use of Potassium Hydrogen Phthalate as a Standard in Alkalimetry.** F. D. DODGE (*J. Amer. Chem. Soc.*, 1920, **42**, 1655—1656. Compare Hendrixson, this vol. ii, 382).—In the preparation of potassium hydrogen phthalate for use as a standard in alkalimetry, it is advisable to crystallise above  $20^\circ$ , because in this way the formation of a more acid salt,  $2KHC_8H_4O_4 \cdot C_8H_6O_4$ , is effectually prevented.

J. F. S.

**Influence of Atmospheric Carbon Dioxide on Alkalimetric Titrations, using Phenolphthalein as Indicator.** G. BRÜHNS (*Zeitsch. Zuckerind. Čechoslov.*, 1920, **44**, 331—335).—Comparative titrations with  $N/100$ -sodium hydroxide and hydrochloric acid solutions, using phenolphthalein and methyl-orange as indicators, showed that, with the former indicator, less acid was required to neutralise a given quantity of the alkali than when methyl-orange was employed. The difference was about 0.5 c.c. per 10 c.c. of acid used, and was due to carbon dioxide absorbed from the atmosphere during the titration.

W. P. S.

**The Significance of the Dissociation Constant in the Identification of Acids and the Detection of Impurities Therein.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 514—518).—The dissociation constant of weak organic acids may be used for their characterisation. This may be conveniently determined by estimating the hydrogen-ion concentration at a given dilution by comparing the colour change of the same indicator in the solution and in a standard solution of known ion concentration. Such standard solutions are represented by very dilute hydrochloric acid or by mixtures of potassium hydrogen phthalate with hydrochloric acid or sodium hydroxide. A selection of suitable indicators is given for various weak acids. The mineral acid or base in a solution of an organic acid may be estimated by measuring the change in the  $p_H$  value of the solution consequent on the addition of a known small quantity of mineral acid or base. The method of calculation is exemplified in the case of tartaric acid. W. S. M.

**The Neutralisation of Weak Acids with Weak Bases and the Examination of the Purity of Ammonium Salts of Weak Acids.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 787—796).—The exact titration of a weak acid with a weak base

is practicable if a suitable indicator is chosen, the choice of the latter being determined by the hydrogen-ion concentration of the resulting salt solution; that is, the  $p_H$  value to which it is desired to titrate must be determined beforehand. An expression,

$$[H^+] = \sqrt{K_{H_2O} \cdot K_{HA} / K_{BOH}}$$

is derived giving the hydrogen-ion concentration in terms of the dissociation constants of the weak acid, the weak base, and water. With the help of this equation, the  $[H^+]$  for mixtures of acid and base is calculated, and the neutralisation curve constructed by plotting  $p_H$  against the composition of the mixture. This curve shows an inflexion for the  $p_H$  corresponding with the neutral point. An indicator is then chosen for which the  $p_H$  in the range of colour change is approximately equal to the calculated value. For example, in the titration of ammonium acetate ( $p_H = 7.1$ ), neutral-red with a range  $p_H = 6.8$  to  $p_H = 8.0$  is chosen. Satisfactory results were obtained for ammonia and oxalic acid (neutral-red), ammonia and succinic acid (neutral-red), ammonia and formic acid (methyl-red), and ammonia and salicylic acid (methyl-red). A method for testing the purity of ammonium salts of weak acids is indicated.

W. S. M.

#### Liquid Ammonia-Sodium Method for the Estimation of Halogens in Organic Compounds.

F. B. DAINES and R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1920, **42**, 1573-1579).—It has been pointed out by Clifford (A., 1919, ii, 423) that in some cases there is a considerable formation of cyanide in the estimation of halogens by the liquid ammonia-sodium process. With the object of ascertaining to what extent and in what circumstances this occurs, the reaction has been carried out with 123 organic compounds, some of which did not contain any halogen, and the resulting solutions tested for cyanide. In most cases there was no cyanide present, but in a few, such as chloroform, bromoform, chloral hydrate, and bromal hydrate, considerable quantities of sodium cyanide are formed, according to the equation  $CHBr_3 + NH_3 = HCN + 3HBr$ , whilst acetone, phenylacetone, and cyanoacetic ester also yield cyanide by direct separation. Cyanides are also formed by ethylidene chloride, tetrachloroethylene, and tetrachloroethane. In all these cases, the estimation of the halogen can be carried out by the modification of the method put forward by Clifford (*loc. cit.*). A large number of estimations are recorded which show that this method of analysis is trustworthy. Attempts to use the liquid ammonia-sodium method for the estimation of cyanogen in organic compounds have shown the unsuitability of the process for this purpose, chiefly because of the formation of amines, according to the equation  $CH_3CN + 4NH_3 + 4Na = C_2H_5NH_2 + 4NaNH_2$ . It is a remarkable fact that iodoform does not give cyanide by this process.

J. F. S.

**Use of Alundum Filtering Crucibles.** D. T. ENGLIS (*J. Ind. Eng. Chem.*, 1920, **12**, 799-800).—Soluble salts may be removed from the upper part of an alundum crucible in which a

precipitate has been collected by supporting the crucible in a suitable holder in an ordinary glass funnel, covering the top of the crucible with a rubber stopper, applying suction to the stem of the funnel, and pouring the wash-water into the top of the latter.

W. P. S.

**Chemical Analysis with Membrane Filters.** L. MOSER and KITTL (*Chem. Zeit.*, 1920, **44**, 637—638).—Whilst membrane filters (A., 1918, ii, 307) are useful for the collection of colloidal precipitates, their use in quantitative analysis is limited by the fact that, in spite of the smooth surface of the filter, it is impossible to remove the whole of the precipitate for weighing, since particles of the precipitate appear to become embedded in the membrane (compare also A., 1919, ii, 520).

W. P. S.

**Wash-bottle for giving a Continuous Stream of Water.** HANS KLEIN (*Chem. Zeit.*, 1920, **44**, 599).—The mouthpiece of an ordinary wash-bottle is fitted with a length of rubber tubing which may be closed with a spring clip, the "bow" of the clip fitting round the cork of the bottle. The bottle is used in the usual way, the clip being closed when there is a sufficient pressure in the bottle and opened to stop the flow of water from the jet.

W. P. S.

**Apparatus for Evolution Methods of Analysis.** E. R. DOVEY (*Analyst*, 1920, **45**, 330—332).—An apparatus suitable for the estimation of available oxygen in manganese dioxide, sulphur in steel, etc., consists of a reaction flask, the delivery tube of which extends into a test-tube containing the solution for absorbing the evolved gas; the test-tube may in turn be connected with a small U-tube containing a small quantity of absorbing solution. A tube extends to the bottom of the reaction flask, and admits air when the pressure in the flask decreases from any cause. Another apparatus, which may be used for absorbing carbon dioxide in the estimation of carbon in steel by the wet combustion method, consists of a reaction flask fitted with a reflux apparatus; the long stem of a tapered funnel extends through the inner tube of the reflux apparatus to the bottom of the flask. The carbon dioxide is conducted from the top of the reflux apparatus to the bottom of a burette containing barium hydroxide solution and in which a rod fitted with discs is placed (an efficient absorption apparatus). The top of the burette is connected with an aspirator. When the absorption of the carbon dioxide is complete, the jet of the burette is passed through a rubber stopper closing a filter tube, the contents of the burette are filtered, and the barium carbonate washed.

W. P. S.

**The Calibration, Accuracy, and Use of Gas Meters.** AUGUST KROGH (*Biochem. J.*, 1920, **14**, 282—289).—A large recording spirometer for calibrating gas meters is described. When properly handled, wet gas meters are instruments of precision. Motor-driven wet meters acting as pumps and having a constant

water level maintained by a slow current of water are accurate to less than 0.1% at all rates below 1 revolution per minute. When calibrated for more rapid rates, they can be used with almost the same accuracy at rates up to 3 revolutions per minute. The volume per revolution decreases with increasing rate. In wet meters with a constant quantity of water the volume per revolution increases with increasing rate, but can be determined with equal accuracy.

Dry gas meters are on the whole less accurate than wet meters, and when arranged to show the volumes directly in litres their indications are often very inaccurate and cannot be calibrated. They should be arranged to count revolutions. Gas volumes representing fractions of a complete revolution are generally very inaccurately indicated, but the volume corresponding with a whole revolution is a practically constant quantity. Varying rates may cause variations in the volume registered, but at practicable rates the variation is usually within 1%. The calibration of a dry meter changes with age.

J. C. D.

**Estimation of Iodine in Connexion with Studies in Thyroid Activity. III.** E. C. KENDALL [with AVERINA PUGH, F. S. RICHARDSON and C. FORRES] (*J. Biol. Chem.*, 1920, **43**, 149—159).—The method previously described (A., 1912, ii, 864; 1914, ii, 815) is modified to render it applicable to the estimation of iodine in blood and tissue. The modifications consist mainly of the removal of oxidising substances from the phosphoric acid employed by reduction with aluminium, the adjustment of the acidity during boiling, and the use of a small piece of hard coal to facilitate the removal of the added bromine.

J. C. D.

**Estimation of Iodine in Blood and in Animal Tissues. IV.** E. C. KENDALL and F. S. RICHARDSON (*J. Biol. Chem.*, 1920, **43**, 161—170).—The application of the method described in the previous paper, to the analysis of tissues poor in iodine, such as blood, was not practicable until a method of destroying large amounts of organic matter without loss of iodine had been evolved. Destructive distillation of the tissue with about 3% by weight of sodium hydroxide at 300—400° destroys much of the organic matter without appreciable loss of iodine. The charred residue is then extracted with water, and much of the residual organic matter in the brown solution is removed by treatment with barium hydroxide. A second fusion in a small crucible, after evaporation to dryness, effects complete incineration. Special forms of heating chambers for the crucibles are described.

J. C. D.

**Volometric Estimation of Hydrosulphides in the Presence of Sulphides, Thiosulphates, and Sulphites. A.** FÖBER (*Chem. Zeit.*, 1920, **44**, 601).—Sodium hydrosulphide when treated with excess of mercuric chloride solution yields free hydrochloric acid according to the equation  $2\text{NaHS} + 3\text{HgCl}_2 = 2\text{NaCl} + \text{Hg}_3\text{S}_2\text{Cl}_2 + 2\text{HCl}$ ; under similar conditions sodium thiosulphate gives



free sulphuric acid (compare Sander, A., 1916, ii, 111), whilst sodium sulphide gives a neutral solution. By titrating the acidity produced by mercuric chloride before and after the test solution has been treated with zinc carbonate, the quantities of thiosulphate and hydrogen sulphide may be estimated; the other constituents may be estimated as described by Sander (*loc. cit.*). W. P. S.

**Estimation of Selenium [in Organic Compounds].** Franz WREDE (*Zeitsch. physiol. Chem.*, 1920, 109, 272—275).—The method here described is based on that given by Pregl for the estimation of sulphuric acid ("Die quantitative organische Mikroanalyse," 1917, 122), and consists in burning the substance in a tube in oxygen in presence of platinum as catalyst and titrating the selenious acid formed with centinormal sodium hydroxide solution, sodium hydrogen selenite being neutral to methyl-orange. [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

**Estimation of Ammonia in Urine [with Remarks on the Technique of the Micro-Kjeldahl Method].** Ludwig PINCUSOHN (*Biochem. Zeitsch.*, 1919, 99, 267—276).—The urine is heated in the distilling flask of a modified micro-Kjeldahl apparatus at 45° with sodium carbonate, and the ammonia is aspirated into a receiver containing standard sulphuric acid and is estimated either by titration or colorimetrically. The time taken for the distillation of the ammonia (ten minutes) is not sufficiently long to allow the conversion of the urea into ammonia. S. S. Z.

**Estimation of Phosphorus in Small Quantities of Blood and Blood-serum.** Poul IVERSEN (*Biochem. Zeitsch.*, 1920, 104, 22—29).—The author describes a modification of Neumann's method (A., 1903, ii, 243), which admits of the estimation of phosphorus in small volumes of blood or serum (compare Feigl, A., 1919, i, 138). T. H. P.

**Titrimetric Estimation of Phosphoric Acid by Neumann's Method.** Poul IVERSEN (*Biochem. Zeitsch.*, 1920, 104, 15—21).—In this method for estimating phosphorus in organic substrata (A., 1903, ii, 243), the organic matter is destroyed by means of sulphuric and nitric acids, the phosphate formed precipitated as ammonium phosphomolybdate, and the latter washed with ice-cold water, which is filtered; the filter and precipitate are then treated with slightly more  $N/2$  sodium hydroxide solution than is necessary to dissolve the precipitate, and the ammonia thus liberated boiled off and estimated by titration: (c.c. of  $N/2\text{-NaOH}$ )  $\times$  0.5539 = amount of phosphorus in milligrams. Gregersen (A., 1908, ii, 64) found it to be necessary to over-titrate with 0.5—1 c.c. of acid and to boil to expel carbon dioxide. Heubner (A., 1914, ii, 675), who dissolves the precipitate on the filter by means of the standard sodium hydroxide solution, gives, however, a higher factor than the above, namely, 0.57. The author shows that Gregersen's

modification gives good results, provided that the excess of  $N/2$ -NaOH taken is at most 4 c.c., and is subject to no systematic error; the mean value of the factor is found, from twenty-five analyses, to be 0.5526 (compare Kleinmann, this vol., ii, 634).

T. H. P.

**Estimation of Phosphoric Acid in Phosphates of the Heavy Metals.** F. SEELIGMANN (*Chem. Zeit.*, 1920, 44, 599).—The phosphate (10 grams) is heated at 90–95° for fifteen minutes with 12 grams of sodium hydroxide solution (D 1.383), the mixture diluted with 4 parts of water, boiled, cooled, diluted to 1 litre, filtered, and an aliquot portion of the filtrate acidified with acetic acid and titrated with uranyl acetate solution. W. P. S.

**Estimation of Phosphoric Acid. I.** (1) The Estimation of Phosphoric Acid as Magnesium Ammonium Phosphate and the Hindrance of its Precipitation by the Serum Constituents. (2) The Estimation of Phosphoric Acid as Uranium Phosphate and as Silver Phosphate. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 19–45).—Serum constituents, such as potassium dihydrogen phosphate, urea, glycine, or calcium carbonate, do not influence the precipitation of phosphoric acid as magnesium ammonium phosphate. The presence of sodium chloride in certain concentrations, on the other hand, leads to high results. Reagents, such as picric acid and trichloroacetic acid, employed in the precipitation of proteins influence the precipitation, although they do not hinder it. Serum does not contain any substances which are capable of preventing the complete precipitation of phosphoric acid as magnesium ammonium phosphate. On precipitating 1 mg. of  $P_2O_5$  as magnesium ammonium phosphate in 50–75 c.c. of solution, 0.006 mg. remains unprecipitated. With a smaller quantity (0.1 mg.) of  $P_2O_5$  the unprecipitated fraction is even proportionately higher. The uranium acetate method yields good results with quantities as low as 10 mg. of  $P_2O_5$ . Quantities below 10 mg. give untrustworthy results. With Liebermann's silver phosphate method high results are obtained, whilst the estimation of phosphoric acid as the vanadium-phosphoric acid-molybdenum complex is found satisfactory. Columbium and tantalum produce no specific coloration with phosphoric acid and molybdenum. S. S. Z.

**Estimation of Phosphoric Acid. II.** The Estimation of Phosphoric Acid in Phosphomolybdates. Gravimetric and Colorimetric Methods. HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 45–95).—The precipitation of molybdenum by Raper's method gives too high values. Preliminary colorimetric experiments have shown that the coloured compounds produced by molybdenum with tannin or the phenols are entirely unsuitable for quantitative analysis. The phenylhydrazine compounds yield untrustworthy results, but the molybdenum-red reaction (potassium thiocyanate) is satisfactory. The most suitable results are obtained with potass-

ium ferrocyanide. One mg. of molybdenum was estimated in 100 c.c. with an error of 0.5%. The procedure was successfully applied for the colorimetric estimation of phosphoric acid, which was precipitated as phosphomolybdate and the molybdenum then estimated colorimetrically with potassium ferrocyanide; 0.1 mg. of  $P_2O_5$  can be estimated by this method with an error of 0.5%. An attempt to devise a satisfactory method for the estimation of ammonium in the phosphoric acid molybdenum complex failed. S. S. Z.

**Estimation of Phosphoric Acid. III. The Estimation of Phosphoric Acid in Phosphomolybdates. Volumetric and Sedimetric Methods.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 95—115).—Low results were obtained with Neumann's method for the estimation of phosphorus when the theoretical factor was used. By washing the ammonium phosphomolybdate precipitate with 50% alcohol instead of water, better results were obtained. In micro-Neumann estimations it is more satisfactory to wash the precipitate than to centrifuge it, as a certain amount of loss is thus obviated. The author describes a "sedimetric" method by means of which the phosphorus is rapidly estimated by measuring the volume of the precipitate after centrifuging it in a graduated tube. The height of the ammonium phosphomolybdate precipitate is proportional to its  $P_2O_5$ -content. S. S. Z.

**Estimation of Phosphoric Acid. IV. The Estimation of Phosphoric Acid as a Strychnine-Phosphoric Acid-Molybdenum Compound (Nephelometry). The General Principles of Nephelometry and the Construction of a New Nephelometer.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 115—150).—A description of the development of nephelometry. A new nephelometer and its manipulation are also described.

S. S. Z.

**Estimation of Phosphoric Acid. V. The Estimation of Phosphoric Acid as a Strychnine Phosphoric Acid-Molybdenum Compound. Special Phosphoric Acid Nephelometry and a New Method of Preparation of the Strychnine-Molybdenum Reagent.** HANS KLEINMANN (*Biochem. Zeitsch.*, 1919, 99, 150—190). Strychnine sulphate and sodium molybdate react in moderately concentrated hydrochloric acid solution to form a clear, colourless, stable reagent, which is suitable for the estimation of phosphoric acid; 0.1–0.0005 mg. of  $P_2O_5$  can be estimated in this way by a nephelometric method with an error of 0.5%. S. S. Z.

**Estimation of Minute Quantities of Arsenic by Titration.** H. H. GREEN (*J. S. African Assoc. Anal. Chem.*, 1920, 3, 3–4).—For quantities of arsenic trioxide ranging from 0.05 to 5 mg., the solution containing the arsenic is treated as usual in a Marsh apparatus and the evolved gases are passed successively through a vessel

containing lead acetate solution and three vessels containing dilute silver nitrate solution. The contents of the silver nitrate vessels are then mixed, treated with sodium hydrogen carbonate, solid potassium iodide is added until the precipitated silver iodide has redissolved, and the mixture is titrated with  $N/500$ -iodine solution. Each c.c. of the latter is practically equivalent to 0.1 mg. of arsenic trioxide. The black silver precipitate need not be removed before the titration is made.

W. P. S.

**Electrometric Analysis of Arsenicals.** CHARLES S. ROBINSON and O. B. WINTER (*J. Ind. Eng. Chem.*, 1920, 12, 775—778).—The electrometric apparatus used is essentially that described by Hillebrand (A., 1913, ii, 721), except that a mechanical stirrer is added and a reflecting galvanometer of the box type employed in place of the capillary electrometer. The titration of arsenic trioxide is made with iodine solution in the presence of sodium hydrogen carbonate, whilst arsenic pentoxide is titrated at 35° in 50% sulphuric acid solution with sodium iodide solution. The method is particularly suitable for the estimation of arsenic in coloured solutions.

W. P. S.

**Estimation of Carbon Dioxide in Carbonates Insoluble in Water.** C. S. ROBINSON (*Soil Sci.*, 1920, 10, 41—47).—Estimations were made of the carbonate content of samples of limestone, marl, and soil. The first method used was that of Van Slyke (A., 1919, ii, 78). The second method was a gasometric one, originally proposed for soluble carbonates by Van Slyke (A., 1917, ii, 422). A special form of cup nitrometer was used, with a tube and special stopper holding the weighed sample introduced between the end of the nitrometer and the levelling tube, which contained mercury. The apparatus having been freed from air, hydrochloric acid was introduced from the cup. After all the gas was evolved, its volume was measured and its weight calculated from tables prepared for the conditions of the determination. The gasometric method was the more accurate of the two, but the first method was to be preferred for samples low in magnesium carbonate.

J. H. J.

**Micro-method for the Estimation of the Carbon Dioxide of the Blood.** A. KROGH and G. LILJESTRAND (*Biochem. Zeitsch.*, 1920, 104, 300—315).—Various modifications are introduced into Barcroft and Haldane's method for estimating the carbon dioxide of the blood (A., 1902, ii, 424); 0.25–0.3 c.c. of blood suffices for two estimations, the mean error of the result being  $\pm 0.5\%$  by volume.

T. H. P.

**Estimation of Potassium and Sodium Present Together.** A. QUARTAROLI (*Gazzetta*, 1920, 50, ii, 64—69).—The disadvantages of the ordinary methods for estimating separately potassium and sodium may be overcome by converting the weighed mixture of the chlorides into nitrates and determining the melting

point of the mixed nitrates, first alone, and, secondly, after admixture with an equal weight of pure potassium nitrate; the melting-point curve falls sharply from  $336^{\circ}$  ( $\text{KNO}_3$ ) to  $220^{\circ}$  (about 55%  $\text{KNO}_3$ ), and then rises sharply to  $306^{\circ}$  ( $\text{NaNO}_3$ ). If  $P$  represents the weight of the mixed chlorides and  $a$  the percentage of potassium nitrate in the mixed nitrates, as indicated by the melting point, then the weight of potassium chloride in the weight  $P$  of mixed chlorides will be given by  $x = 1.0723aP / (0.0723a + 100)$ . [See also *J. Soc. Chem. Ind.*, 1920, October.] T. H. P.

**Estimation of Total Calcium in Soils and the Significance of this Element in Soil Fertility.** O. M. SHEDD (*Soil Sci.*, 1920, 10, 1—14).—A more rapid and accurate method than that already in use for the estimation of calcium in soils, and one in which the production of an ammonia precipitate, which occludes calcium, is avoided, is described. One gram of the sample is fused with fusion mixture and the silica separated in the usual manner. The filtrate is made just alkaline with ammonia, and then just acid with hydrochloric acid, heated to the b. p., and precipitated with 1—2 grams of solid ammonium oxalate. The mixture is kept on the steam-oven for a few hours, and then at the ordinary temperature overnight. The precipitate is filtered and ignited. The oxide or carbonate is dissolved in hot dilute hydrochloric acid, and bromine water and ammonia added to precipitate manganese. The solution is acidified with acetic acid, and the manganese filtered off. The filtrate is then reprecipitated as before.

Analyses by this method of a large number of soils, both cultivated and uncultivated, showed that cultivation led to a considerable loss of calcium. The more fertile soils contained the most calcium. The application to soils poor in calcium of limestone or rock phosphate is beneficial, on account of the calcium they supply as plant food, apart from any other benefit they confer.

J. H. J.

**Estimation of Calcium in Small Quantities of Blood Serum.** BENJAMIN KRAMER and JOHN HOWLAND (*J. Biol. Chem.*, 1920, 43, 35—42).—One or 2 c.c. of serum are evaporated to dryness in a platinum crucible and gently incinerated. The ash is dissolved in a small quantity of  $N$ -hydrochloric acid, and the solution again evaporated to dryness and incinerated. The crystalline residue is readily soluble in not more than 1 c.c. of 0.1*N*-sulphuric acid, and this solution is quantitatively transferred to a special type of 2 c.c. calibrated tube. After neutralisation by ammonia and warming, the calcium is precipitated by an excess (0.3 c.c.) of 0.1*N*-oxalic acid in 0.05*N*-sulphuric acid. The reaction must be acid at this point. Heating is continued for a few minutes, 0.1 c.c. of a saturated solution of sodium acetate is added, the tube is well shaken, and the volume is made up to 2.0 c.c. After several hours, the precipitate is filtered through a hardened filter, and the excess of oxalic acid in 1 c.c. of the filtrate is estimated by titration with 0.01*N*-potassium permanganate. A

blank estimation on the reagents is necessary. The method appears to be trustworthy.

The results previously reported by Howland and Marriott (A., 1918, ii, 21) on the calcium of the serum in infantile tetany are confirmed. J. C. D.

**Use of Organic Solvents in the Quantitative Separation of Metals. III. Separation of Magnesium from Sodium and Potassium Chlorides.** S. PALKIN (*J. Amer. Chem. Soc.*, 1920, 42, 1618—1621. Compare A., 1917, ii, 43).—The method previously published for the separation of lithium from sodium and potassium (*loc. cit.*) has been modified and adapted to the separation of magnesium from sodium and potassium. The modified method depends on a progressive precipitation of the sodium and potassium chlorides from a concentrated solution by the use of alcohol and ether, and is divided into two stages: (i) in which all but a few milligrams is precipitated, and (ii) in which the last few milligrams are removed from solution. The estimation is carried out as follows: the total chlorides of magnesium, sodium, and potassium are dissolved in the minimum quantity of water (about 1.5 c.c. of water are sufficient for 0.5 gram of substance), one drop of concentrated hydrochloric acid is added, and gradually 25 c.c. of absolute alcohol are dropped into the liquid while rotating. The sodium and potassium chlorides should precipitate in a uniform granular condition. In a similar manner, 25 c.c. of ether are added, and the mixture is kept until the precipitate is agglomerated and the supernatant liquid nearly clear. The mixture is filtered, and the beaker and precipitate are washed with a mixture of one part of alcohol and four parts of ether. The filtrate is evaporated to dryness on a steam-bath; the residue is dissolved in 10 c.c. of alcohol, one drop of concentrated hydrochloric acid added, and the mixture warmed until practically everything has dissolved. The beaker is then rotated and 50 c.c. of ether slowly added, and the mixture kept for twenty minutes. The precipitate is collected on the same filter, washed with the ether-alcohol mixture, dried, ignited, and weighed. The filtrate containing the magnesium is evaporated nearly to dryness, dissolved in 5—10 c.c. of concentrated hydrochloric acid and a little water, sodium hydrogen phosphate is added, and the estimation completed in the usual way. The method has several advantages over the usual method, namely, (i) it affords a direct estimation of the sodium and potassium salts, inasmuch as they are precipitated first rather than after the magnesium, (ii) the reagents used are volatile organic solvents, and (iii) no foreign salt or base is introduced as a precipitating agent. J. F. S.

**Magnesia Mixture.** O. KUHNT (*Chem. Zeit.*, 1920, 20, 586).—If "magnesia mixture" is prepared without the addition of ammonia, it may be kept for an indefinite period in glass bottles without the glass being attacked, with the consequent formation of a precipitate in the reagent. The absence of ammonia does not

interfere with the use of the reagent for the precipitation of phosphoric acid; only a slight excess of the reagent should be employed, and ammonia added subsequently in sufficient quantity.

W. P. S.

**Estimation of Small Amounts of Copper by the Iodide Method.** H. F. BRADLEY (*J. Ind. Eng. Chem.*, 1920, 12, 800).—

The precipitate of cupric sulphide is washed, moistened with a few drops of concentrated zinc nitrate solution, and ignited. The residue of oxides is dissolved in dilute hydrochloric acid (1:1), the solution neutralised with 5% potassium hydroxide solution, acidified with acetic acid, a small amount of phosphate solution is added, followed by 2 grams of sodium iodide, and the liberated iodine is titrated.

W. P. S.

**Estimation of Mercury in Urine.** R. FABRE (*J. Pharm. Chim.*, 1920, [vii], 22, 81-85).—

One litre of the urine is heated under a reflux apparatus with 100 c.c. of hydrochloric acid, and 6 grams of potassium chlorate are added in small quantities at a time during a period of about two hours. The solution is boiled under the reflux apparatus to expel the greater part of the free chlorine, cooled, treated with sulphur dioxide, and again boiled. After filtration, the solution is treated with 15 c.c. of stannous chloride solution, heated for two hours on a water-bath, and at the end of twenty-four hours the liquid is decanted from the grey precipitate. The latter is treated with a few c.c. of hydrochloric acid to cause the mercury to collect in a globule, which is washed with water, alcohol, and ether, dried over sulphuric acid, and weighed. If the quantity of mercury is very small, it may be collected on a gold-coated asbestos filter, as recommended by

W. P. S.

**Some Microchemical Methods.** ALFRED BRAMMALL (*Geol. Mag.*, 1920, 57, 123-125). The following microchemical tests for iron and manganese are described. (1) *Detection of iron*: The cover

glass is removed, and the slide is cleansed of balsam, polished, again cleansed, and warmed. Reaction paper is prepared by soaking pieces of white drawing paper in concentrated hydrochloric acid and pressing them in similar sheets until no longer wet. An ammonium thiocyanate paper is similarly prepared. The acid paper is carefully laid on the section, covered with a strip of cardboard on which is laid a hot iron for two or three minutes. After the slide has dried, the thiocyanate paper is similarly applied, pressed in the cold, and again dried. The distribution of ferric iron is revealed by a transparent blood-red stain of ferric thiocyanate. Potassium ferrocyanide similarly used gives an opaque blue coloration which must be examined in reflected light. The method was found valuable in the examination of the "spotted rocks" of Andlauthal, Vosges; of dark inclusions in, and alterations of chistolite: lamination in shales; identification of magnetite, siderite, etc. (2) *The fusion test for man-*

... applied to slides as follows: A slide is ground down

and one side polished. The slide is then detached from the glass slip, and cleansed from balsam and dried. It is allowed to soak for several minutes in a hot saturated solution of potassium carbonate and nitrate and dried. A thin wash of the solution is applied to the polished surface and allowed to dry. This surface is subjected to the f. p. tip of the blowpipe flame for a few minutes, and after cooling is slightly polished to level the veneer of the fusion. After remounting on the slide with the prepared surface downward, the section is ground thin and examined by transmitted light. (3) *Obscure bedding planes and minute structures in chalk and limestone* may be revealed by differential solution of ground and polished sections in a bath of carbonated waters, a method approximating to weathering.

CHEMICAL ABSTRACTS.

**The Adsorption of Copper Oxide and Nickel Oxide by Precipitates of Ferric Oxide.** ER. TOPORESOU (*Compt. rend.*, 1920, 171, 303—305).—By the addition of ammonium hydroxide to a solution of a ferric salt containing in addition either a copper salt or a nickel salt a certain amount of copper oxide or nickel oxide is always adsorbed by the ferric hydroxide, the amount depending on the relative proportions of the two salts present and the amount of ammonium hydroxide added. These oxides cannot be removed from the ferric oxide by washing the precipitate or by treatment with concentrated ammonia solution.

W. G.

**Analysis of Zirconium Minerals.** H. V. THOMPSON (*Pottery Gaz.*, 1920, 45, 767).—In the analysis of zirconium ores two main difficulties are encountered: (1) raw zirconium ores and products manufactured therefrom are not easily decomposed, and (2) the separation of aluminium from zirconium is not readily effected. Use is made of the fact that after fusion with sodium peroxide and decomposition of the fusion with water, the residue contains all the iron, titanium, and zirconium in the form of oxides together with some of the silica, whilst the whole of the aluminium and the remainder of the silica are contained in the filtrate. This process possesses the advantage that zirconium and aluminium are automatically separated during the decomposition of the sample.

CHEMICAL ABSTRACTS.

**Differential Analysis of Acetone, Acetaldehyde, and Formaldehyde in Organic Liquids.** EMILIO PITTARELLI (*Arch. farm. Sper. sci. Aff.*, 1920, 29, 70—87).—The various methods, depending on precipitation, coloration, or odour, for the detection of acetone, acetaldehyde, and formaldehyde are described and discussed as regards their application to fermented liquids, milk, urine, etc. In the examination of urine, the free acetone may be separated by treatment with excess of Nessler's reagent, and the combined acetone by distilling the filtrate with an acid. T. H. P.

**Colour Reaction of Milk in Presence of Formaldehyde.** ARTURO ROSSI (*Boll. Chim. Farm.*, 1920, 59, 265—268).—The pres-



ence of formaldehyde in milk may be detected by adding 2—2.5 c.c. of the milk carefully to 2 c.c. of sulphuric acid (D 1.820—1.825) in a test-tube, so that the liquids mix as little as possible, and then shaking the tube rapidly; the liquid assumes a more or less intense violet colour, according to the proportion of formaldehyde present. The best conditions for the reaction vary with such proportion, the sensitiveness diminishing with more than 0.0005% of the aldehyde; in doubtful cases the samples to be tested may be diluted with pure milk. Other substances may be examined for formaldehyde by subjecting them to distillation, mixing part of the distillate with pure milk, and applying the sulphuric acid reaction. Milk free from formaldehyde sometimes gives this violet coloration, but only after being in contact with the sulphuric acid for some hours. T. H. P.

**Estimation of Minute Amounts of Acetone by Titration.** ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 43—56).—A modification of the Messinger titration method suitable for dilute solutions of acetone. The conditions necessary for an accurate estimation have been carefully worked out and are fully described.

A method of successive distillation from acid, alkaline, and oxidising solutions is described, whereby acetone may be separated from much larger amounts of alcohol and other interfering substances. J. C. D.

**Estimation of Acetone in Expired Air.** ROGER S. HUBBARD (*J. Biol. Chem.*, 1920, **43**, 57—65).—The patient breathed for five or ten minutes through a mask or through a mouthpiece, the expired air passing through two bottles containing 75 c.c. of a freshly prepared 2.5% solution of sodium hydrogen sulphite. For the removal of interfering substances the contents of the bottles were distilled successively with 10% sodium hydroxide solution, acidified potassium permanganate solution, and a solution of sodium peroxide. In the final distillate, acetone is estimated either by the method described above (preceding abstract) or by the turbidity method, using the Scott-Wilson reagent. J. C. D.

**Determination of Micro-reduction.** D. G. COHEN TERVAERT (*Zeitsch. physiol. Chem.*, 1920, **110**, 41—54).—The experiments here described show that Bang's modified method for the micro-estimation of sugar in blood (*A.*, 1918, ii, 278, 279; this vol., ii, 199; compare also Maclean, *A.*, 1916, i, 613; 1919, ii, 434) is applicable only when the liquid is heated for a definite time.

The author describes a simple method, consisting in oxidation by means of chromic acid, which allows of the estimation of dextrose, lactose, and maltose. As measured by this method, the reduction of the blood is higher than is indicated by the ordinary copper methods. Dextrose added to blood is estimated quantitatively by this method. T. H. P.

**Micro-estimation of Dextrose by Bang's Method.** BERTHOLD OPLER (*Zeitsch. physiol. Chem.*, 1920, **109**, 57—64).—The author has tested this method (this vol., ii, 199) with quantities

of pure dextrose varying from 0.545 mg. to 0.027 mg., the ratio between the weight of dextrose (mg.) and the number of c.c. of 0.01N-iodate solution increasing from 1:2.78 to 1:1.19, whereas Bang and Hatlehoel (A., 1918, ii, 279) gave the constant value 1:2.8 for this ratio. No greater constancy of this ratio is achieved by the use of steam for boiling the solution. Hence, for the estimation of dextrose in the blood an empirical table is necessary. It is questionable if Bang's method really suffices for the estimation of sugar in a few drops of blood, and for the estimation of 1 mg. or less of dextrose, Bertrand's method is recommended. T. H. P.

**Estimation of Minimal Quantities of Dextrose, specially in Blood.** H. C. HAGEDORN and B. NORMAN JENSEN (*Ugeskrift for Læger*, 1918, 80, 1217—1228).—The method, which gives concordant results, depends on the precipitation of proteins by zinc hydroxide, the reduction of potassium ferricyanide by dextrose, and the iodometric estimation of the excess of ferricyanide. Blood, 0.1 c.c., is added to a mixture of 5 c.c. of 0.45% hydrated zinc sulphate solution and 1 c.c. of N/10-sodium hydroxide, the mixture is heated in a boiling water-bath for four minutes, cooled, and filtered; the tube, precipitate, and filter are washed thrice with 3 c.c. of water. Two c.c. of a solution (1.649 grams of potassium ferricyanide and 28.6 grams of sodium carbonate decahydrate in one litre, which will keep in the dark for at least two months) are added and the mixture is heated in a boiling water-bath for fifteen minutes. After cooling, 3 c.c. of a solution (5 grams of potassium iodide, 10 grams of hydrated zinc sulphate, and 50 grams of sodium chloride in 200 c.c.) and 2 c.c. of 3% acetic acid are added, and the mixture is titrated with thiosulphate (1.24 grams of hydrated sodium thiosulphate in one litre, which must be standardised against potassium ferricyanide or 0.005N-potassium iodate). The difference between 2 c.c. and the volume of thiosulphate used is the volume of ferricyanide reduced by dextrose, the amount of which is determined by the following figures, in which the volume of ferricyanide in c.c. is followed by the amount of dextrose in mg.: 0.10, 0.017; 0.20, 0.035; 0.30, 0.053; 0.40, 0.070; 0.50, 0.088; 0.60, 0.106; 0.70, 0.124; 0.80, 0.141; 0.90, 0.159; 1.00, 0.177; 1.10, 0.195; 1.20, 0.214; 1.30, 0.232; 1.40, 0.251; 1.50, 0.270; 1.60, 0.290; 1.70, 0.310; 1.80, 0.331; 1.90, 0.355; 2.00, 0.384.

## CHEMICAL ABSTRACTS.

**Improved Method for the Detection of Sugar, particularly in Urine.** WALTER S. HAINES, GILBERT P. POND, and RALPH W. WEBSTER (*J. Amer. Med. Assoc.*, 74, 301—302; from *Chem. Zentr.*, 1920, iv, 240—241).—A modified Haines solution is recommended, for which copper sulphate (5 grams), glycerol (250 c.c.), potassium hydroxide (20 grams), or sodium hydroxide (14.3 grams) are dissolved in 1 litre with distilled water. The copper sulphate is dissolved in a warm mixture of water (250 c.c.) and glycerol (250 c.c.); the alkali is dissolved separately in water

(200 c.c.), after which the solutions are mixed and made up to 1000 c.c. Five c.c. of the solution are heated to boiling and treated in an inclined test-tube with 10—20 drops of urine, the phosphate of which has been precipitated and filtered after addition of 5—6 drops of sodium hydroxide solution (5—10%). A red or yellow ring is immediately formed at the junction of the solution and urine if the latter contains more than 0.1% of sugar; if only 0.03% is present, the ring only appears after a few seconds, but, at any rate, within a minute. Smaller amounts of sugar, which then lie within physiological limits, cannot be detected, so that a positive result of the test indicates a pathological condition. H. W.

**Iodometric Estimation of the Phenyl Derivatives of Arsenious Acid.** PAUL FLEURY (*Bull. Soc. chim.*, 1920, [iv], 27, 699—704).—In continuation of previous work (this vol., i, 578) a method has been devised for estimating arsenic trichloride, phenyl-dichloroarsine, diphenylchloroarsine, and triphenylarsine in a mixture of the four compounds.

A benzene solution of the mixture is extracted with aqueous sodium hydroxide, whereby arsenious acid and phenylarsenious acid are extracted. This extract is acidified with hydrochloric acid until its acidity is approximately  $N/10$ , alcohol is added in equal volume, and the mixture is titrated with standard iodine solution. The iodine used is equivalent to the phenyldichloroarsine present in the original mixture. An excess of sodium hydrogen carbonate is added, and the titration is again completed. The further amount of iodine required is equivalent to the arsenic trichloride originally present. The benzene solution left after the extraction with alkali is titrated with standard iodine solution, the amount required being equivalent to the diphenylchloroarsine and triphenylarsine originally present. To the product from this titration an excess of aqueous sodium hydrogen carbonate is added, and the whole is extracted with chloroform. The chloroform extract contains triphenylarsine oxide, and if the aqueous solution is now acidified and again extracted with chloroform, the second extract will contain diphenylarsenic acid, which may be obtained in a crystalline form on evaporation of the solvent. W. G.

**Estimation of Volatile Acids in Fermentation Products.** G. HINARD (*Ann. Chim. Analyt.*, 1920, [iii], 2, 239—242).—Fifty c.c. of the liquid are mixed with 10 c.c. of water and distilled, 50 c.c. of distillate being collected and titrated. Fifty c.c. of water are then added to the contents of the distillation flask, and a second quantity of 50 c.c. is distilled and titrated. These operations are repeated several times and a curve plotted from the results: the asymptote of this curve indicates the amount of alkali solution required to neutralise the total volatile acids present. W. P. S.

**Isolation of Formic, Acetic, and Lactic Acids.** ISENOURA ONODERA (*Ber. Ohara Inst. landw. Forsch.*, 1917, i, 231—259; from *Chem. Zentr.*, 1920, iv, 271).—The three acids are extracted from

the mixed solution by means of ether. In one portion of the ethereal solution formic acid is titrated with permanganate, and, in this oxidised portion, the lactic acid is estimated as oxalic acid. Acetic acid is removed from the decomposed solution by means of ether, and the extract is again distilled. The method is trustworthy, and its accuracy is not influenced by the presence of small amounts of propionic and butyric acids.

H. W.

**The Colorimetric Estimation of Tyrosine by the Method of Folin and Denis.** ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 1678—1692).—Tyrosine cannot be estimated quantitatively in the products of protein hydrolysis by means of the phenol reagent of Folin and Denis (*A.*, 1912, ii, 1012). Tryptophan, if present, will give an intense colour with the reagent, and indole and indole derivatives, as well as ferrous salts, also give the blue colour. It seems probable that other products of protein hydrolysis may also produce blue colours with the phenol reagent. Further, in the case of tyrosine itself the depth of colour varies with the relative proportion of reagent and tyrosine present, the colour values falling off sharply as the concentration of the tyrosine increases. Protein hydrolysates must not be decolorised with carbon or bone charcoal if they are to be used subsequently for the estimation of amino-acid content, as tyrosine, tryptophan, and its decomposition products are adsorbed in appreciable amounts by bone-black. Bone-black itself contains some easily oxidisable material, which dissolves in acid solutions and then gives the blue colour with the phenol reagent.

W. G.

**Estimation of Uric Acid by Clarification of the Liquids by means of Talc.** E. LAMBLING and C. VALLÉE (*Compt. rend. Soc. Biol.*, 1920, **83**, 793—795; from *Chem. Zentr.*, 1920, iv, 217).—A portion of the uric acid is carried down by talc even from acid solutions.

H. W.

**Analytical Characters of Dichlorodiethyl Sulphide.** FELIX MARTIN (*J. Pharm. Chim.*, 1920, [vii], **22**, 161—165).— $\beta\beta'$ -Dichlorodiethyl sulphide ("mustard gas"), after oxidation, gives the usual reaction for sulphuric acid. When a small quantity of the substance is heated with alcoholic potassium hydroxide solution, and the vapours produced are passed into Denigès's reagent (an acid solution of mercuric sulphate), a white precipitate is formed; if the vapours are absorbed in water, the solution, on treatment with a drop of iodine solution, yields an odour similar to that of mercaptan. Dichlorodiethyl sulphide is hydrolysed by water, and the solution yields a turbidity when treated with Grignard and Rivat's reagent (iodine 8 grams, gum arabic solution 1 c.c., copper sulphate 0.8 gram, and water 33 c.c.).

W. P. S.

**Behaviour of Phenolphthalein with Iodine and a Method for the Estimation of Phenolphthalein.** SAMUEL FALKIN (*J. Ind. Eng. Chem.*, 1920, **12**, 766—769).—Investigation of the

action of iodine on phenolphthalein relative to the conditions governing the formation of tetraiodophenolphthalein and the physical properties of the latter, yielded information on which was based the following method for the estimation of the substance. The phenolphthalein is dissolved in 30% potassium hydroxide solution and a small quantity of water, 20 grams of ice are added, and then an excess of iodine reagent (10% of iodine in 15% potassium iodide solution, the free iodine being then combined by the addition of alkali). Concentrated hydrochloric acid is now added until precipitation is complete, more iodine is added if the liquid is not brown in colour, the precipitate is dissolved by the addition of 30% potassium hydroxide solution, and the precipitation and solution repeated three or four times. The final alkaline solution is treated with 0.5 c.c. of 10% sodium sulphite solution, acidified with hydrochloric acid, and extracted several times with acetone-chloroform mixture (1:3); the united extracts are evaporated, the residue of tetraiodophenolphthalein dried at 100°, and weighed. The weight multiplied by 0.3781 gives the amount of phenolphthalein present.

W. P. S.

**Estimation of Codeine.** H. E. ANNETT and HARIDAS SEY (*Analyst*, 1920, **45**, 321—328).—The following method may be applied to opium, pure alkaloids, plant materials, etc., with suitable modification of the amounts of substance taken. Ten grams of dry opium are mixed thoroughly with 4 grams of calcium hydroxide and 100 c.c. of water, the mixture stirred for thirty minutes filtered, and 50 c.c. of the filtrate are treated with 40 c.c. of 2% acetic acid and 10 c.c. of basic lead acetate solution (D 1251). After filtration, 75 c.c. of the filtrate are shaken with 2 grams of calcium hydroxide for thirty minutes, the mixture filtered, and 50 c.c. of the filtrate are extracted with three successive quantities of 50 c.c. of toluene. The combined toluene extract is filtered and treated with dry hydrogen chloride, avoiding any great excess of the latter. Codeine hydrochloride separates, and, after excess of hydrogen chloride has been expelled by a current of air, is collected, dissolved in water, the solution evaporated, and the residue of codeine hydrochloride dried and weighed. W. P. S.

**Colour Tests for Nitrates and Nitrites, Antipyrine (in Pyramidone), Phenol and Aniline, and  $\alpha$ - and  $\beta$ -Naphthols.** A. ESCAICH (*J. Pharm. Chim.*, 1920, [vii], **22**, 138—141).—The author's colour test for nitrites (A., 1918, ii, 273) gives uncertain results with natural waters rich in chlorides, but the latter may first be removed by means of silver nitrate. When the nitrates of the water are to be reduced to nitrites by amalgamated aluminium, this process must precede the precipitation of chlorides. Magnesium, like aluminium, may be activated by immersion in mercuric cyanide solution and used for reducing nitrates to nitrites. A colour test is described for the detection of antipyrine in pyramidone, based on the production of violet and red colorations by conversion of antipyrine into nitrosoantipyrine, and oxidation

of the latter with lead peroxide. A very sensitive test for phenol in aqueous solutions is to treat 10—15 c.c. with five to ten drops of ammonia, 0.05—0.1 gram of sodium persulphate, and four or five drops of *N*/10-silver nitrate solution. A green coloration is produced, which changes to blue or yellow, according as the concentration of phenol was more or less than about 0.05 gram per litre.  $\alpha$ -Naphthol dissolved in aqueous alcohol and treated with sodium nitrite and a few drops of acid mercuric sulphate solution gives a fine, red coloration and red precipitate, whilst  $\beta$ -naphthol gives a yellow precipitate.

J. H. L.

**Estimation of Phenol in the Presence of certain other Phenols.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1920, 12, 771—775).—The method depends on the red coloration yielded by phenol with Millon's reagent when the mixture is heated in the presence of nitric acid; most other phenols give yellow colorations, but  $\beta$ -naphthol gives a brown, and salicylic acid a red, colour. It is necessary to heat the mixture at 100° for thirty minutes in order to discharge the original red colour given by the other phenols and to allow the red colour of phenol itself to reach its full intensity. Various modifications of the method are described which are suitable for different requirements. The red coloration given by phenol may be reduced to yellow by the action of formaldehyde, whilst any yellow colour present originally is not affected. [See, further, *J. Soc. Chem. Ind.*, 1920, 652A.] W. P. S.

#### Method for the Estimation of Cineole in Eucalyptus Oils.

T. TESTING COCKING (*Pharm. J.*, 1920, 105, 81—83).—Three grams of the eucalyptus oil, dried previously over calcium chloride, are mixed with 2.1 grams of *o*-cresol, and the solidifying point of the mixture is determined. The quantity of cineole present is ascertained by reference to a graph.

W. P. S.

**Estimation of Urea in Blood in Normal and Pathological Cases; Comparative Results of the Hypobromite and Xanthhydrol Methods.** M. LAUDAT (*Compt. rend. Soc. Biol.*, 1920, 83, 730—732; from *Chem. Zentr.*, 1920, iv, 68).—Considerable errors are involved in the estimation of urea in blood by the hypobromite method, since ammonia, uric acid, and creatine are decomposed by the reagent to a greater or less extent. Xanthhydrol, on the other hand, does not attack these substances.

H. W.

**Estimation of Urea in Blood by Xanthhydrol.** W. MESTREZAT and MARTHE JANET (*Compt. rend. Soc. Biol.*, 1920, 83, 763—764; from *Chem. Zentr.*, 1920, iv, 217).—The experimental conditions necessary for an exact estimation have been investigated.

The xanthhydrol method is no longer exact in a 1% solution of urea; Tanret's reagent dissolves xanthylurea. The serum (10 c.c.) is diluted to such an extent that it contains about 0.5 gram of

urea per litre, treated with concentrated Tanret's reagent (10 c.c.), and centrifuged. The clear liquid is treated under definite conditions with pure acetic acid and a 10% solution of xanthhydrol in absolute methyl alcohol; after three hours, the xanthylcarbamide is filtered through a Gooch crucible, washed with absolute methyl alcohol, dried at 70°, and weighed. H. W.

**Estimation of Urea by Xanthhydrol.** FRENKEL (*Ann. Chim. Anal.*, 1920, [ii], 2, 234—239).—Ten c.c. of a 10% solution of urine are treated with 35 c.c. of glacial acetic acid, and 1 c.c. portions of 10% xanthhydrol solution (in methyl alcohol) are added at intervals of ten minutes until 5 c.c. have been introduced. After one hour, the precipitate formed is collected, washed with alcohol, dried at 100°, and weighed; the weight is divided by 7 to obtain the amount of urea. Other substances found in urine do not give a precipitate with the reagent. The method may be applied to the estimation of urea in blood after this has been treated with mercuric chloride-potassium iodide reagent (mercuric chloride 2.71 grams, potassium iodide 7.20 grams, glacial acetic acid 66 c.c., and water 100 c.c.), and filtered. W. P. S.

**Micro-method for the Estimation of Urea in Blood and Organic Secretions.** K. L. GAD-ANDRESEN (*Biochem. Zeitsch.*, 1919, 99, 1—19).—The proteins are precipitated with 0.01N-acetic acid in the presence of sodium acetate, and the urea is estimated in the filtrate with sodium hypobromite. The nitrogen evolved is measured with Krogh's microrespirometer, and the result calculated by means of Krogh's formula. A correction is made for the nitrogen evolved by other substances. Only 0.1 c.c. or 0.15 c.c. of blood is required. The occasional error is of the magnitude of 0.5 mg. per 100 c.c. Comparisons with the urease method showed good agreement. This method is applicable to blood and various secretions of the organism. It is not suitable for the estimation of urea in muscle tissue. S. S. Z.

**Estimation of Hydrocyanic Acid.** R. LEITCH MORRIS (*Pharm. J.*, 1920, 105, 83—85). Liebig's method (titration with silver nitrate solution) is trustworthy for the estimation of hydrocyanic acid provided that the acid is neutralised previously; any great excess of alkali must be avoided, and this is best attained by using borax solution in place of sodium hydroxide for the neutralisation (Guerin's modification). Excess of borax does not interfere. Volhard's method is useful in special cases, but entails the separation of the silver cyanide by filtration before the excess of silver nitrate can be titrated. Mohr's method (titration with silver nitrate after neutralisation with magnesium oxide, and using potassium chromate as indicator), and Denigès' modification of Liebig's method (titration in alkaline solution, using potassium iodide as indicator), are also trustworthy, but in the latter it is essential to use a sufficient quantity of potassium iodide. Fordos and Gelis' iodometric method is suitable for the estimation of cyanide in mercury cyanide. W. P. S.

**Hydrocyanic Acid in *Phaseolus lunatus*.** J. A. SIMPSON (*Anal. Acad. Cien. Med. Fis. Nat. Habana*, 1918—1919, 55, 250—283; *Expt. Sta. Rec.* 42, 7).—To estimate hydrogen cyanide, the crushed beans were heated with dilute sulphuric acid, and the distillate was collected in sodium or potassium hydroxide solution. This was heated with calcium polysulphide and titrated with 5% ferric sulphate until the colour of ferric thiocyanate developed. With care, the method is accurate to 0.00001 gram HCN. Of the varieties examined, "Rangoon blanca" gave 40 mg. HCN per 100 (grams?). Several gave between 3 and 8 mg. per 100 (grams?). The rest gave negative results.

CHEMICAL ABSTRACTS.

**Modification of the Van Slyke Method for Estimating Arginine.** A. E. KOEHLER (*J. Biol. Chem.*, 1920, 42, 267—268).—Van Slyke's method (compare A., 1916, ii, 62) is modified by drawing a slow current of air through the liquid during the digestion, the apparatus for absorbing the ammonia being a simple gas wash-bottle.

W. G.

**Volumetric Estimation of Diazo-compounds by Reduction.** EDMUND KNECHT and LEONARD THOMPSON (*J. Soc. Dyers and Col.*, 1920, 36, 215—219).—Benzenediazonium chloride in dilute hydrochloric acid solution may be titrated with titanous chloride solution, using H-acid as external indicator. The reaction requires two equivalents of hydrogen, and takes place without simultaneous formation of phenylazoimide and aniline. The titration may also be carried out by adding an excess of titanium trichloride solution and titrating the excess with acid-green solution in the presence of sodium tartrate. Methods are also described for the titration of sodium *p*-nitrosodiazobenzene with titanium trichloride solution or sodium hyposulphite solution. [See, further, *J. Soc. Chem. Ind.*, 1920, 594A.]

W. P. S.

**Proteins and Some New Methods of Investigating their Composition.** A. C. ANDERSEN (*K. Vet. Landbohøjskole Aarskrift*, 1917, 308—334; from *Chem. Zentr.*, 1920, iv, 113).—Van Slyke's method of analysing proteins is modified by separating the fifth fraction (amino-nitrogen) into two sub-fractions; the first of these contains glycine, alanine, serine, phenylalanine, tyrosine, valine, and the three isomeric leucines as monoamino-monocarboxylic acids, whilst the second comprises the monoamino-dicarboxylic compounds, aspartic and glutamic acids. When an aqueous solution of a mixture of these amino-acids is neutralised with sodium hydroxide in the manner recommended by Sørensen for the formaldehyde titration, the monoamino-monocarboxylic acids, together with proline and oxyproline, remain uncombined, whilst the monoamino-dicarboxylic acids react with one equivalent of base. After evaporation of such a solution and incineration of the residue, sodium carbonate is left in amount equivalent to the monoamino-dicarboxylic acids present. Exact directions for performing the analyses are given.

H. W.



**The Estimation of Hæmatin in the Whole Blood.** FRED VILKS (*Bull. Soc. chim. Biol.*, 1920, 2, 125—132).—Two methods, depending on the transformation of a mixture of oxyhæmoglobin and hæmatin into one of reduced hæmoglobin and reduced alkaline hæmatin, or one of carboxyhæmoglobin and reduced alkaline hæmatin, respectively, are described. The estimation is carried out by spectrophotometric means. J. C. D.

**A Method for the Estimation of Methæmoglobin and Hæmoglobin in Blood.** W. S. McELROY (*J. Biol. Chem.*, 1920, 42, 297—300).—The total hæmoglobin (methæmoglobin + hæmoglobin) is determined colorimetrically as hæmoglobin, using potassium ferricyanide to convert the hæmoglobin into methæmoglobin. The oxygen capacity is determined by Van Slyke's method (compare A., 1918, ii, 82), from which is calculated the hæmoglobin. The difference between the two values is the amount of methæmoglobin. W. G.

**A Quantitative Method for Estimation of Vitamine.** ROGER J. WILLIAMS (*J. Biol. Chem.*, 1920, 42, 259—265. Compare A., 1919, i, 463).—It has been shown that the number of yeast cells produced from a single cell in eighteen hours under given conditions is a measure of the amount of vitamine present (compare Bachmann, A., 1919, i, 613). The method is now modified, and is gravimetric. A culture solution containing 20 grams of sucrose, 3.0 grams of ammonium sulphate, 2.0 grams of potassium phosphate, 1.5 grams of asparagine, 0.25 gram of calcium chloride, and 0.25 gram of magnesium sulphate in 1 litre of water is prepared. To 100 c.c. of this solution a known amount of the solution to be tested is added, and the mixture is made up to 110 c.c. and pasteurised or sterilised. To this is added 1 c.c. of freshly made yeast suspension containing 0.3 gram of fresh yeast per litre, and the whole is incubated for eighteen hours at 30°. A little formaldehyde is added to stop growth, any growth of wild yeast on the surface is removed by a copper gauze scoop, and the yeast is then filtered off on a Gooch crucible, washed with water, dried at 103° for two hours, and weighed. The weight of yeast thus obtained minus the weight obtained in a control is directly proportional to the amount of vitamine added. The results are expressed as a "vitamine number," this being the number of milligrams of yeast produced by 1 gram of the material tested. It has been shown by experiment that nothing except vitamine in the small amounts used will materially improve the medium, which already contains asparagine in addition to ammonium sulphate. W. G.

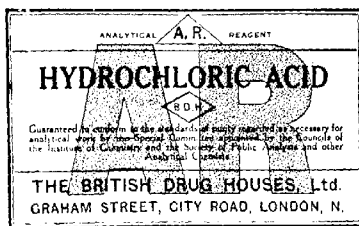
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